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16. ABSTRACT

The use of industrial boilers for the destruction of hazardous wastes is increasing at a rapid rate. This is partly due to the fact that the practice changes a "negative value" waste material into a "positive value" fuel and partly to the fact that current RCRA regulations specifically exempt facilities that burn wastes in energy producing operations from complying with RCRA incineration mandates. This study evaluated the concept with the purpose of answering the following questions:

- What is the present and projected magnitude of hazardous waste combustion in boilers.
- Which waste materials and boiler types are the most compatible, and what quantities of these are available.
- What are the potential mechanical difficulties or environmental hazards associated with this practice

The major conclusions were:

- Cofiring of many hazardous wastes in watertube boilers, especially those whose temperatures exceed 1100°K (1500°F) with a furnace residence time exceeding 1 second appears feasible and environmentally safe for many wastes
- Conditions in firetube boilers do not appear to be sufficient to destroy many hazardous compounds.
- These are preliminary findings based on literature data and theoretical considerations, further testing is required.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report documents a recently completed feasibility study to determine whether industrial boilers could potentially be used for safely destroying hazardous wastes. The study compares the theoretical conditions needed to destroy certain hazardous materials with conditions found in typical industrial boilers. The results suggest that boilers can achieve requisite levels of hazardous waste destruction and that further work in this area could be fruitful. If field data can support the conclusions drawn from these theoretical analyses, boilers could become an acceptable method of hazardous waste disposal. For further information contact the Incineration Research Branch, IERL, Cincinnati, Ohio.

David G. Stephan, Director
Industrial Environmental Research
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ABSTRACT

The present Resource Conservation and Recovery Act permits the firing of hazardous waste materials in industrial boilers when the wastes are used as supplementary fuel. This report presents an evaluation of the cofiring of hazardous wastes as fuel in industrial boilers. The information presented includes a review of the rate of generation of hazardous wastes which are candidates for such use, and the present and projected future extent of the use of boilers for this purpose. Also presented is an inventory of industrial boilers, standard boiler characteristics, and the temperature-time profiles of each boiler studied. Theoretical temperature-time requirements for destruction of hazardous wastes are compared to those expected in industrial boilers to assess whether the boiler is an appropriate vehicle for waste destruction. There are many key variables that must be considered in the use of this type of model. Examples of these are degree of waste fuel atomization, variation of gas residence times from the mean furnace residence time, temperature variations from the bulk stream temperature across any furnace cross section, and effects of boiler load changes. The general conclusions are that expected variations in these variables are sufficient to warrant careful evaluation of waste streams and boiler combinations before reaching firm conclusions on the environmental safety of cofiring hazardous wastes as fuel. An overview of the elements for a complete evaluation of this potential disposal technology is presented.

This report was submitted in fulfillment of Contract Number 68-03-2567, Task 4034, of the U.S. Environmental Protection Agency. This report covers a period from September, 1980 to October, 1981.

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SECTION 1

INTRODUCTION

1.1 BACKGROUND

Approximately 40 million metric tons of hazardous wastes are currently generated annually in the U.S. On May 18, 1980, the Environmental Protection Agency (EPA) promulgated Phase I rules and interim status standards regulating the generation, transporation, treatment, storage, and disposal of these wastes under authority of the Resource Conservation and Recovery Act (RCRA). These and subsequently announced regulations place stringent restrictions on generators of wastes, including requirements for manifesting wastes and chain-of-custody liability. These restrictions may ultimately impose additional costs on the waste generator for offsite disposal. Thus, economic incentives for disposing of wastes onsite may result.

One method of disposing of wastes with high organic content is by thermal destruction. This can be done by high-temperature incineration, which is regulated by RCRA. However, another means of thermal destruction is by cocombustion of the waste, or use of the waste as a fuel (if its heating value is sufficiently high), in devices whose primary purpose is energy production, such as boilers and process heaters.

Current RCRA regulations specifically exempt facilities that burn wastes in energy-producing operations from complying with RCRA incineration mandates. In fact, it is estimated that about 20 million metric tons of wastes that might be classified as hazardous, owing to their characteristics, are currently burned as fuel, or cocombusted with fuel, in energy-producing operations.

The purpose of this study is to provide a basis for answering several key questions:

- What is the present and projected magnitude of hazardous waste combustion or cocombustion in boilers?
- Which waste materials and boiler types are the most compatible?
- Are there potential mechanical difficulties or environmental hazards associated with waste combustion in boilers?

The opportunity for combustion of hazardous wastes in industrial boilers is greater than currently practiced. There are over 40,000 industrial boilers in the U.S. with capacities greater than 10 million Btu/hr. These units offer great potential for hazardous waste combustion.

Regulations published on January 23, 1981, for incineration of hazardous wastes require 99.99-percent destruction and removal efficiencies (DRE) for the principal hazardous organic constituents in the waste incinerated. If the temperature-time profile of a given boiler type is similar to the time and temperature required to destroy a given waste, then the disposal of the hazardous waste in the boiler can become an option open for more extensive evaluation. This evaluation would consider the compatibility of the primary fuel to the waste, potential impacts on the design conditions of the boiler, retrofit requirements, and fugitive and secondary emissions. This report presents information on each of these issues.

1.2 SCOPE OF THIS STUDY

As previously noted, the objective of this study is to assess the problems and potential of destroying hazardous wastes in industrial boilers. The major elements of this overview include:

- Surveying hazardous waste generation and disposal practice
  - -- Document present generation and disposal inventories
  - -- Establish the present extent of waste combustion as fuel
  - -- Project the future extent of waste combustion as fuel

- Assembling an inventory of industrial boiler capacity capable of hazardous waste combustion
  - -- Inventory by size, design type, and fuel fired
  - -- Provide regional inventories
  - -- Select a set of model boilers typifying the installed population

- Characterizing the combustion characteristics of typical boilers
  - -- Establish boiler operating and design characteristics
  - -- Establish boiler temperature-time profiles as a function of boiler characteristics

- Characterizing hazardous wastes suitable for combustion
  - -- Specify the requirements (temperature and time) for waste constituent destruction
  - -- Define the composition of candidate wastes and rank the listed waste streams for potential use as fuel

- Identifying the matrix of wastes/boiler types suitable for hazardous waste combustion
  - -- Combine boiler combustion characteristics with waste constituent destruction requirements
  - -- Specify boilers/wastes achieving 99.99-percent destruction

- Provide an overview of considerations for further evaluating the waste/boiler destruction option

Results and findings associated with each of these elements as they address the objectives of the study are discussed respectively in Sections 3 through 8 of this report. Conclusions and recommendations of the entire study are summarized in Section 2.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

As discussed in the introduction, the primary purpose of this study was to determine whether hazardous wastes could potentially be safely destroyed under the conditions found in a number of industrial boilers. The study determined that the thermal destruction requirements of most wastes evaluated are satisfied by the conditions found in a large percentage of industrial boilers currently in use. However, because of the nature of such a theoretical evaluation, it can only be concluded that boilers appear to have the potential for safe waste destruction. Further experimental work is necessary to confirm this conclusion. In this respect this study represents only a starting point for more detailed technical evaluation of industrial boilers as vehicles for the safe disposal of hazardous wastes. This study did establish that further work is warranted and could result in significant benefits in both expansion of safe, hazardous waste disposal capacity and the utilization of the energy content that wastes represent.

2.1 CONCLUSIONS

The conclusions developed from this theoretical analysis are:

- Cofiring of hazardous wastes at a small percentage of the base fuel (about 5 to 10 percent) appears to be a viable method of disposing of most hazardous organic material.
- Cofiring many wastes, or firing some high Btu content wastes entirely may produce lower levels of criteria pollutant and trace element emissions than either traditional coal or oil combustion.
- The conditions found in many types of watertube boilers appear to be sufficient to achieve at least 99.99 percent destruction of most hazardous organic compounds.
- The conditions found in firetube boilers do not appear to be sufficient to destroy all hazardous organic materials. There is too great a likelihood that cold tube-wall quenching of the waste degradation reactions is possible before complete destruction can occur.
- Watertube boilers whose furnace exit temperatures are greater than 1,100K (1,500°F) and whose furnace mean residence times are greater than 1 second appear to be best candidates for the destruction of simple hazardous organic waste streams.
- Complex organic waste streams are likely to require approximately 200K (360°F) higher temperatures.

- Insufficient data are available to predict whether hazardous products of combustion could be released from a boiler. Laboratory data should, however, be able to provide some conservative estimates of the likelihood of the release of such materials. The formation of hazardous products of combustion must be addressed by further research.
- In the absence of other data, the autoignition temperature appears to be a possible predictor of the relative ease of a compound's thermal destruction. This needs further confirmation.

2.2 RECOMMENDATIONS

This study showed that certain boilers can theoretically destroy hazardous organic materials. This work suggests the following areas of further research which need to be addressed:

- The available waste destruction kinetic data are based on results obtained from thermal destruction analytical system (TDAS) experiments. While such work is very useful, it does not model the destruction phenomena that occur in a flame. This type of information must now be obtained through a flame-mode destruction apparatus.
- The current TDAS work (as well as future flame-mode work) needs to be broadened to include destruction characteristics of the wastes under the pyrolytic (no oxygen) as well as under high oxygen concentration conditions. Further information on the formation and destruction of hazardous products of combustion is also needed.
- The information that will be obtained by EPA under the hazardous waste manifest system needs to be evaluated to determine other wastes which are potential candidates for destruction in boilers.
- A field program needs to be initiated to verify the preliminary results of this study. The program should include testing of the full boiler system, not just the boiler's emissions. The tests should include:
    - Full input/output analysis of all streams.
    - Boiler temperatures at a number of points in the combustion chamber
    - Boiler residence time variations.
    - Testing for the principal organic hazardous components in the waste and for hazardous products of combustion. TDAS data can be used to determine which products of combustion could occur and hence should be tested for.

SECTION 3

SURVEY OF HAZARDOUS WASTE GENERATION AND DISPOSAL

This section presents data on the rate of generation of hazardous wastes, the current practice of disposal in industrial boilers, and the future of this practice as impacted by regulatory and consumer activities.

3.1 HAZARDOUS WASTE GENERATION

Estimates of the quantities of hazardous wastes generated in the U.S. have been developed over recent years and documented in a wide variety of available literature. Studies ranging from in-depth industrywide surveys to studies presenting well-defined and specific segments of an industry provide valuable data on the type of hazardous wastes generated and the location of the generators. Information developed in recent reports, (Ref. 1-4) were the most pertinent data sources for quantifying hazardous waste inventories.

A 1980 report (Ref. 1) presented a brief overview of inventory data available from a variety of federal and state studies completed over the past several years. Although many of these efforts have been quite extensive, the ultimate disposal fate, and knowledge of quantities of hazardous wastes generated are still limited to estimation. The data compiled from the state surveys varied widely from state to state in level of detail and reliability, but many states have completed extensive surveys to determine quantities of wastes generated, waste types, and disposal practices of generators.

With the recent implementation of RCRA, each state must re-evaluate its methods of estimating the volume and determining the disposal practices of the hazardous waste generators. Even then, the basis of quantities will not be consistent since some states may have more stringent regulations than those required by RCRA. As an example, federal legislation contains a small generator exclusion. California has no small generator exclusion, thereby increasing the number of generators contributing to the hazardous waste inventory.

The definition of hazardous waste is the single most important factor in determining waste quantities and generators. Recent changes in EPA's list of hazardous components and hazardous waste definitions have impacted the values used in this report and those from the most recent Agency inventories (Ref. 5).

The data available from federal studies ranges from overview information, such as the assessment of hazardous waste practices in various industries (Ref. 6-8), which were conducted in the mid-1970's by EPA's Office of Solid Waste (OSW), to more specialized studies done on specific topics related to hazardous waste assessment and disposal.

3.1.1 Summary of Hazardous Waste Generated by EPA Region

Table 1 presents estimates of total quantities of hazardous waste generated by manufacturing industries in the U.S. by EPA region. These values were obtained using the best method available to estimate the total quantities of hazardous waste generated. They were based on the assumption that the ratio of the amount of hazardous waste generated by an industry to the number of employees in that industry is approximately constant for each plant in each industry (as grouped at the SIC code level). The table gives estimates of the quantities of hazardous waste generated within 17 of the 19 standard industrial classification (SIC) codes comprising the manufacturing industry, and one nonmanufacturing code. The stated values have limited reliability because of a lack of consistent and comprehensive site-specific data.

Since the RCRA regulations do not differentiate between wastes amenable to thermal destruction and those not amenable, quantities given in Table 1 include both. Therefore, to determine the quantities of waste potentially available for thermal disposal, the wastes which are primarily inorganic must be factored out. The remaining, primarily organic, wastes are called class A here. Of these wastes, the fraction containing high Btu material is called class B.

For class A (organic) hazardous wastes, the quantity of organic waste generated was determined by multiplying an estimate for the fraction of organic material contained in a given industry's waste (characterized by SIC code) by the generation rate of that industry's waste for each geographical area. These fractions were determined from quantities of waste reported in state inventories (Ref. 9-12) and an EPA waste report (Ref. 13). When quantitative values were not available, organic contents listed as high, large, low, or negligible were assigned values of 80, 50, 30 or 5 weight percent, respectively. The organic fractions used in subsequent calculations by SIC code are:

TABLE 1. SUMMARY OF HAZARDOUS WASTE GENERATED BY EPA REGION (1,000 METRIC TONS PER YEAR) (REF. 2)

		EPA Region											
	SIC code	I	II	III	IV	V	VI	VII	VIII	IX	X	Total	Percent of total
22	Textile mill products	27	24	4	132	10	6	0	0	0	0	203	0.5
24	Lumber and wood products	4	3	7	20	10	8	3	2	9	21	87	0.2
25	Furniture and fixtures	2	4	4	9	7	2	2	0	5	1	36	0.1
26	Paper and allied products	130	272	130	156	324	77	52	13	117	25	1,296	3.1
27	Printing and publishing	11	25	19	19	38	10	11	4	13	3	153	0.4
28	Chemicals and allied products	185	1,497	2,515	8,763	1,870	8,577	553	1	1,426	123	25,510	62.0
29	Petroleum and coal products	0	122	165	90	384	878	99	61	258	61	2,118	5.1
30	Rubber and miscellaneous plastics products	22	28	22	39	83	17	11	2	22	2	248	0.6
31	Leather and leather products	156	57	24	14	137	0	38	5	38	5	474	1.1
32	Stone, clay, and glass products	1	2	1	3	4	2	1	1	2	1	18	0.1
33	Primary metal industries	2	185	791	434	1,348	452	74	109	101	565	4,061	9.8
34	Fabricated metal products	204	212	172	172	781	137	96	28	164	31	1,997	4.8
35	Machinery, except electrical	26	31	28	29	127	24	20	6	28	4	323	0.8
36	Electric and electronic equipment	67	156	183	82	334	65	28	5	145	27	1,092	2.6
37	Transportation equipment	86	73	80	106	464	80	80	13	199	60	1,241	3.0
38	Instruments and related products	14	21	8	6	21	3	3	2	11	1	90	0.2
39	Miscellaneous manufacturing industries	48	66	24	42	72	18	12	7	24	6	319	0.8
40	Nonmanufacturing industries	119	335	177	237	414	177	118	59	276	59	1,971	4.8
	TOTAL[a]	1,104	3,113	4,354	10,353	6,428	10,533	1,201	318	2,838	995	41,237	100.0
	Percent of total	2.7	7.5	10.6	25.1	15.6	25.5	2.9	0.8	6.9	2.4	100	

[a] Totals may not balance because of rounding of numbers.

SIC code	Organic content (weight percent)	SIC code	Organic content (weight percent)	SIC code	Organic content (weight percent)
20	80	27	30	33	30
22	80	28	70	34	50
23	30	29	40	35	50
24	80	30	80	36	30
25	50	31	80	37	30
26	50	32	50	38	50
				39	30

The class A hazardous wastes listed in Table 2, along with quantities generated, represent the best candidates for thermal disposal. The values were obtained by multiplying the waste quantities for each SIC code (Table 1) by the assigned organic content, and totaling.

Class B (highly combustible) hazardous wastes, a subset of the class A wastes presented in Table 2, represent wastes with the highest heat content. The heat content of these is sufficiently high to support combustion. A study (Ref. 14) provided the basic industry data for compiling the quantity of class B wastes generated. The class B waste quantities identified in SIC codes 28 and 29, (by far the largest contributors to the waste class) were distributed among the region based on the regional generation of waste within that code. For example, from Table 1, 185,000 metric tons of SIC 28 waste were generated in Region I. This represents 0.73 percent of the SIC code 28 waste. Therefore, 0.73 percent of the SIC 28 generated class B total was assigned to Region I. The distribution of the wastes other than for the SIC codes 28 and 29 was determined using the total waste percentages shown at the bottom of Table 1.

The OSW generator notification information, as required by RCRA, and now available only on a limited basis, is expected to provide better estimates of waste generation rates. The number of industries that have to date notified EPA that they generate a hazardous waste is shown in Table 3. Further information on the two types and quantities of hazardous waste generated is unavailable at this time.

3.1.2 Options For Disposal of Hazardous Waste Based on State Inventory Data

Data on the amount of hazardous waste disposed of by the various available methods are presently unavailble. However, a comprehensive and recent (1979) industrial hazardous waste generation and disposal inventory is available for the State of New York (Ref. 9). Using this data base, representative values and approaches to quantifying the hazardous waste volumes that could be burned in boilers were developed. Such values are

TABLE 2. SUMMARY OF HAZARDOUS WASTE GENERATED BY EPA REGION (1,000 METRIC TONS PER YEAR)

	EPA Region										
	I	II	III	IV	V	VI	VII	VIII	IX	X	Total
Total hazardous waste EPA inventory[a] (Table 1)	1,104	3,113	4,354	10,353	6,428	10,533	1,201	318	2,838	995	41,237
Organic wastes class A[b]	550	1,621	2,390	6,735	3,002	6,778	627	105	1,490	369	23,668
Highly combustible wastes class B[c]	19	109	173	535	176	570	45	7	112	19	1,765

[a] Summary of hazardous waste is the OSW estimated values developed by multiplying regional employment figures for each SIC code times waste generation factors.

[b] Class A: Organic quantities were determined by averaging the organic fraction of hazardous waste for each two-digit SIC code and multiplying by the OSW estimated total hazardous waste for that industry segment in each region. These product values were added for each region.

[c] Class B: Highly combustible quantities were determined by selecting a limited set of industrial wastes (those useful for steam generation and having unit quantities) determined by Acurex based partly on Reference 14 and distributed to various regions on a basis of specific industry waste generation (SIC codes 28, 29, or all segments).

TABLE 3. NUMBER OF HAZARDOUS WASTE GENERATORS PER EPA REGION[5]

EPA Region										
I	II	III	IV	V	VI	VII	VIII	IX	X	Total
3,370	5,260	5,080	6,920	9,800	8,270	2,270	1,570	4,315	1,500	48,355

presented as an example since nationwide values could only be determined by having such data from all states.

Of the 1.12 million metric tons of hazardous wastes inventoried in New York, 0.56 million metric tons were disposed onsite by the following methods:

Disposal method	Metric tons per yr
Distillation	48,610
Incineration	94,040
Reclaimed for fuel or material value	148,780
Other (landfill, lagooning, storage, neutralization)	
Total	560,600

The organic fraction of materials in the "other" category (mostly solvents, oils, and still bottoms) was 15,800 metric tons. In addition, wastewater treatment sludge, mixed waste, and lagoon bottoms also contained combustible organic materials. In total, the organic waste categories constitute about one-half of the total hazardous waste material.

Table 4 lists the major hazardous waste generating industries in New York, including those generating nonorganic type wastes. The total quantity of waste tabulated in Table 4 represents greater than 86 percent of the total (all industry) quantity of hazardous wastes generated in New York.

The New York survey also categorized wastes by type as shown in Table 5. Of these wastes, types that can be incinerated include halogenated solvents, other solvents, waste oils, still bottoms, leather tanning waste, and some wastewater treatment sludges. By reviewing the industries contributing to the wastewater sludge category, it was estimated that the organic content of

TABLE 4. MAJOR HAZARDOUS WASTE GENERATING INDUSTRIES IN THE STATE OF NEW YORK (REF. 11)

Type	Approximate hazardous waste generation (metric tons)	Percent of total from survey
Inorganic chemicals	61,250	5.5
Organic chemicals, pesticides, and explosives	290,314	25.9
Miscellaneous chemicals	12,095	1.1
Primary metals	200,012	17.8
Pharmaceuticals	105,900	9.4
Plastics and rubber	105,601	9.4
Leather tanning and finishing	54,438	4.9
Motor vehicles and equipment	44,983	4.0
Photographic chemicals and equipment	40,207	3.6
Machine manufacturing	38,109	3.4
Electroplating and metal finishing	13,534	1.2
Total	966,443	86.2

TABLE 5. VOLUMES OF HAZARDOUS WASTES BY TYPE IN THE STATE OF NEW YORK (REF. 11)

Type	Approximate hazardous waste generation (million liters)[a]	Percent of total from survey
Acids	72.0	7.7
Alkalies	9.0	1.0
Pickle liquor	55.0	5.9
Etching solution	4.0	0.5
Halogenated solvents	4.0	0.4
Other solvents	192.0	20.6
Heavy metal sludges	55.0	5.8
Wastewater treatment sludges	198.0	21.3
Other sludges	63.0	6.8
Waste oils	57.0	6.4
Still bottoms	12.0	1.4
Photographic chemicals	7.0	0.8
Rinse water and other wastewaters	45.0	9.3
	773.0	
Subtotal	982,270 metric tons	
Leather tanning wastes	54,445 metric tons	4.9
Total	1,036,720 metric tons	92.8

[a] Use 1.12 kg/liter to convert to metric tons.

wastewater sludge was 42 volume percent. When this quantity was added to the organic content of the other components, the combustible waste fraction totalled 477,000 metric tons or 43 percent of the total waste quantity generated in the state. The total quantity of these waste types represents over 92 percent of the total hazardous waste listed in the New York survey.

The most significant factors illustrated by this case study are the large quantity of combustible hazardous waste (over 43 percent of the total), the large number of generators that dispose of waste onsite (over half), and the prominence of industries that usually have onsite boilers. Such a study which provides site-specific data on wastes and boilers represents the only method that can be used to quantify the amount of material that could be boiler destroyed if plant operators so choose. If the inventory had separately reported the use of reclaimed material for fuel, the information would be more helpful. However, this inventory provides more exact estimates of hazardous waste that could be used for fuel in boilers than the current EPA RCRA background data (Ref. 2,3).

Such an estimation would utilize the various classes of waste given, stream size, and industry type, and correlate these values with characteristics provided in the literature (Ref. 7,8,15) and boiler availability. While an estimate of the extent of hazardous waste destruction in boilers for the state of New York is not carried out here, this site-specific data show that the quantities of waste which are potentially boiler-disposable are considerably higher than estimates based on general industrywide waste estimates would predict. The primary reason that such inventory data are more useful is the inclusion of quantities of combustible types of wastes. In the case of the data from New York, the extent of solvent waste disposal is much higher than most available data would indicate. Thus, at least some state data indicate that the potential for boiler destruction could be higher than generally expected.

3.2 CURRENT PRACTICE OF DISPOSAL OF HAZARDOUS WASTE IN INDUSTRIAL BOILERS

Though the destruction of hazardous materials in steam boilers and space heaters has occurred randomly at various locations, only limited cases are reported in the literature. In those industries where the practice has gained widespread acceptance, the wastes are generally classified as fuels and not hazardous wastes. Therefore, this survey includes destruction in industrial boilers of hazardous wastes as defined in 40 CFR Part 261 of RCRA, as well as those hazardous wastes exempt from RCRA because of their fuel value. For example, waste oil burned for fuel is exempt from RCRA though it would potentially be classified a hazardous waste if it were disposed of. Waste material fuels not included in this survey include waste gas and biomass (wood, bark, bagasse, food processing products, other undegraded cellulosic materials).

Several studies have been conducted on the reuse or disposal of waste materials in combustion processes. Recent assessments (Ref. 1,14) are the most pertinent to this effort. Also, another recent study (Ref. 4) listed waste materials burned for energy for several industries. Other literature

(Ref. 16,17) amplify data on air emissions or cofiring conditions for similar waste destruction.

Quantification of hazardous waste disposal in boilers includes several groups of waste categories described below. They include: (1) waste-oil firing, (2) pulping-waste firing (3) petroleum refining fuels, and known individual plant burning of other hazardous wastes.

3.2.1 Waste Oil

Excess spent oils contaminated by metal, dirt, water, or organic solids and liquids represent a major hazardous waste material. An estimated 9,458 million liters of oil are used yearly in the U.S. (see Table 6). Since 1960, the quantity of waste that has been re-refined has decreased from a peak of 1,136 million liters to an estimated 189 million liters in 1977. Less severe processing practices than re-refining (see Table 7) are estimated to condition over 379 million liters/yr, generating some 40,000 metric tons of sludge and tank bottoms. Anticipated new re-refining equipment may reverse the decreasing trend and produce higher re-refined oil sales in the 1980's (Ref. 15). Simultaneously, more sludge and bottom deposited materials will be generated.

Currently waste oil boiler feed is estimated as follows:

	Million liters/yr
Direct use as fuel	1,360 (high percent to boilers)
Processing plant fuel	185 (high percent to boilers)
Sold for fuel	2,350 (high percent to boilers)
Total	3,895
Reclaimable waste oil:	
Other uses of reclaimable oil	
Re-refined oil	314
Process waste	273
	587
Fuel	3,895
Total	4,478

Comparable other study values were 4,200 million and 4,700 million liters/yr.

TABLE 6. WASTE OIL INVENTORY (MILLION LITERS PER YEAR) (REF. 18)

Waste oil generation	Million liters
Automotive lubricating oil	2,332
Industrial and aviation lubricating oil	1,491
Other industrial oil	329
U.S. government lubricating oil	68
Marine oil, transportation losses, oil spills	791
Other oil losses in production and transportation	4,375
Subtotal	9,386
Oil and fat industry losses	49
Coke oven oil losses	23
Total generated	9,458
Ultimate disposal	
Directly to environment	3,702
Processing waste to environment	273
Road oil dust control	1,064
Subtotal environment	5,039
Directly for use as fuels	1,355
Used for processing plant fuels	185
Fuels sold by oil processors	2,350
Subtotal fuels	3,890
Road oil and dust control, lost by biodegradation	144
Re-refined oil sales	314
Subtotal other	458
Unknown	72
Total disposal	9,458

TABLE 7. WASTE LUBE OIL RECYCLING METHODS

Reclaiming	
Removes	Water, solids
Process	Heat 100°0 to 180°OF Separatory screening Demulsification Gravity settling or centrifugation
Products	Fuel Parting agents, e.g., concrete forms
Reprocessing	
Removes	Water, solids Additives blended with original oil Compounds formed during use
Process	Heat 150°0 to 200°OF Chemical treatment, acid, caustic, sodium silicate Surfactants (demulsification, solids settling) Gravity settling or centrifugation Separatory screening Filtration
Products	Fuel Noncritical lubricants Parting agents
Re-refining	
Removes	Water, solids Original additives Compounds formed during use Light ends (low boiling fractions) Color bodies and soluble high boiling compounds
Process	Chemical pretreatment (similar to reprocessing) Distillation 550°0 to 650°OF Clay contact Filtration
Products	Distillate fuel Lubricating oils Motor oils Hydraulic oils Machining oils Process oils

Since the above values are typical of 1971 oil usage, a growth factor has been applied to obtain 1980 values. During 1965 to 1975, oil usage increased 11 percent for segments with high reclaimable oil, an annual growth rate of 1.1 percent. Using this growth rate from 1971 to 1980 gives a 9.9 percent increase. The 1971 value of 3,891 million liters yields a 1980 estimate of 4,300 million liters/yr or 4.1 million metric tons.

3.2.2 Waste Chemical Pulping Liquors

Chemical pulping of wood is generally carried out under highly acidic or alkaline conditions and usually produces both a pulp product and spent liquor byproduct. Spent liquors from the alkaline sodium process (Kraft pulping) are evaporated and burned for pulping chemical (and energy) recovery. Sulfite (acid) spent liquors traditionally were disposed by lagooning or wastewater discharge until regulation in the 1950's and 1960's stopped this practice. Most of these latter wastes are now concentrated, burned, or neutralized and sold as concrete additives, oil drilling mud components, and other byproducts. Table 8 presents the pertinent yield factors for various pulping wastes. An estimated 5.3 million metric tons of solids are currently burned (at 65 percent solids) in boilers as the primary fuel with supplemental oil-firing mechanisms.

3.2.3 Petroleum Refining Onsite Waste Burning

Current petroleum refinery production has been estimated to be 16 million bbl/day nationally (Ref. 20). A highly variable fraction of this process material is burned as fuel (frequently fired in boilers) or discharged as process waste. Details of the various wastes are given by Rosenberg et al.(Ref. 6). Although the report is very comprehensive in its coverage of industry practices, no use of materials for energy generation were identified (by definition fuel was exempt). To determine the amount of material burned in boilers, the quantity of fuel was estimated with exclusions for gases and crude oil firing. Utilizing a net liquid fuel use factor of 0.875 percent, the total tonnage burned in boilers is estimated at 7.64 million metric tons/yr nationwide.

3.2.4 Industry Waste Solvent Burning for Energy

Waste solvents generated by the organic chemicals industry are routinely reclaimed as solvent, distilled (also for reclaimed solvent), used for fuel, or incinerated. Other disposal methods such as landfill with residues or storage account for a smaller fraction. Harrison et al. (Ref. 1) has noted the high energy recovery potential of these wastes but found that only a small fraction of the solvents were reclaimed. Several state inventories have included burning of solvents as a specific disposal method, thereby quantifying the disposal in boilers and heaters (Ref. 9,10).

End uses of solvents from degreasing operations include reclamation of 45 percent, while 15 percent is mixed with waste oil (most of which is used as fuel) (Ref. 21). Similar percentages were reported by the State of Massachussets (Ref. 10). These values are higher than an earlier reported

TABLE 8. FACTORS DETERMINING PULPING HAZARDOUS WASTES DESTROYED IN BOILERS

			Fiber production (1,000 tons)				Waste quantity burned	
Pulp type	Yield	Waste per unit of fiber	1972[a]	1980 Projection	Waste solids 1980	Fraction burned as waste	1,000 tons/yr	1,000 metric tons/yr
Dissolving	0.36	1.78	1,677	1,720	3,062	0.95	2,909	2,645
Sulfite	0.48	1.08	2,130	1,980	2,138	0.80	1,710	1,555
Neutral sulfite semichem	0.72	0.39	3,800	4,200	1,638	0.75	1,228	1,116
							5,847	5,315

[a] Reference 19.

2 percent (Ref. 22). In New York, detailed solvent disposal inventories indicated that most waste solvents were generated by SIC code 28 industries and about 26 percent of these were burned for fuel. Most state inventories do not identify material burned for fuel, thus, the New York data may be the best available. The solvent component in SIC 28 hazardous wastes ranged from 1 to 50 percent in state inventories (Ref. 9,12,23-25). A value of 20 percent of all SIC code 28 industry hazardous wastes was assumed to represent the quantity of solvent. Using 26 percent as the amount of solvent used for fuel, a factor for total hazardous wastes burning as fuel of 5 percent was calculated (0.20 x 0.26 = 0.052). Although this factor may be low for many areas, it amounts to over 1.4 million metric tons of the estimated 28.6 million metric tons of SIC code 28 industry waste generated nationally.

3.2.5 Miscellaneous Waste Firing Examples

Although not quantifiable, a variety of other industries are known to dispose of small amounts of organic waste in boilers. These include plywood (condensed hydrocarbon residues), wood processing (wastewater sludge), textile manufacturing (liquid waste), and petrochemical plants (liquids). Specific examples are shown in Table 9.

3.2.6 Summary of Current Practice

From the above waste generator categories, approximately 19 million metric tons/yr of organic waste materials are estimated to be fired in industrial boilers as fuel. This breaks down as follows:

Fuel source	Quantity (million metric tons)	Estimated accuracy
Waste oils	4.1	±30%
Industry solvents	1.4	Inaccurate
Pulping waste liquors	5.3	±5%
Petroleum refining	7.6	Unknown
Textile/petrochemical liquids	0.4	Unknown
Miscellaneous plants	Undetermined	--
Total	18.8	

Acknowledging that many of the above fuels are commonly accepted as traditional fuels rather than wastes, they are included as defined earlier. In all cases except petroleum refining, these materials were wasted to the environment before environmental pressure or handling costs in addition to

TABLE 9. LIQUID ORGANIC WASTE STREAMS CURRENTLY DISPOSED IN BOILERS (REF. 4)

Composition	Source	Producer	Location	Process	Product	Flowrate (kg/hr)
ND	Low-boiling overheads	Tennessee, Eastman	Kingsport, TN	Ketone	Acetic anhydride	ND
Organics	Heavies removal column	Union Carbide	Brownsville, TX	n-Butane oxidation	Acetic acid, formic acid, methyl ethyl ketone, ethyl acetate, acetic anhydride	ND
Organics	Propionic column	Union Carbide	Brownsville, TX	n-Butane oxidation	Acetic acid, formic acid, methyl ethyl ketone, ethyl acetate, acetic anhydride	ND
Organics	Butyl removal column	Union Carbide	Brownsville, TX	n-Butane oxidation	Acetic acid, formic acid, methyl ethyl ketone, ethyl acetate, acetic anhydride	ND
Organics	Ethyl acetate refining column	Union Carbide	Brownsville, TX	n-Butane oxidation	Acetic acid, formic acid, methyl ethyl ketone, ethyl acetate, acetic anhydride	ND
Light ends	Light ends refining column	Union Carbide	Brownsville, TX	n-Butane oxidation	Acetic acid, formic acid, methyl ethyl ketone, ethyl acetate, acetic anhydride	ND

ND = No data

(continued)

TABLE 9. (continued)

Composition	Source	Producer	Location	Process	Product	Flowrate (kg/hr)
Acetaldehyde volatiles	Distillation	Union Carbide	Taft, LA	Oxidation	Acrolein	129
Water, oxygen, carbon, hydrogen, ash	Waste oil stream from refining	DuPont	Orange, TX	Cyclohexane	Adipic acid	8,600
Water, oxygen, carbon, hydrogen, ash	Waste oil stream from refining	DuPont	Victoria, TX	Cyclohexane	Adipic acid	8,600
Cyclohexanone, 0.5%, cyclohexane, 32% phenol, 8.5% heavies, 59%	Heavy ends	Union Carbide	Taft, LA	Phenol	Cyclohexanol, cyclohexanone	88
High boiling organics	Adiponitrile purification	Monsanto	Decatur, AL	Adiponitrile	Hexamethylene diamine	ND
Low boiling organics	Adiponitrile purification	Monsanto	Decatur, AL	Adiponitrile	Hexamethylene diamine	ND
High boiling organics	Hexamethylenediamine purification	Monsanto	Decatur, AL	Adiponitrile	Hexamethylene diamine	ND
ND	Residual tars	Union Carbide	Institute, WV	Chlorination	Linear alkylbenzene	143
Methanol, 70%; water, 8%; other organics, 22%	Extraction and refining	Tenneco	Houston, TX	High pressure	Methanol	1,224
Water, 25% organics, 70% methanol, 5%	Spent catalyst	Union Carbide	Institute, WV	Methanol hydro-chlorination	Methyl chloride	0.05
Organic polymers	Secondary butyl alcohol purification and water extraction	ARCO Chemical	Channel View, TX	Secondary butyl alcohol	Methyl ethyl ketone	253

ND = No data

increasing fuel costs, encouraged their use as fuel. In all cases, spills or improper alternative disposal could cause adverse environmental damage.

3.3 PROJECTED TRENDS IN HAZARDOUS WASTE DISPOSAL IN INDUSTRIAL BOILERS DURING THE PERIOD 1980 TO 1985

Many factors will influence the future use of industrial boilers for the disposal of hazardous wastes. These include the compatibility of the waste material and boiler type (see Sections 6 and 7), emission and hazardous waste disposal regulations, byproduct recovery potential, and other economic and technical considerations (see Section 8).

The sensitivity of projected degrees of waste disposal are dependent on each of the above factors. Using the waste categories discussed in the previous section, these same materials are evaluated to establish the projected change in quantities disposed of in industrial boilers.

Boiler disposal of groups of waste is expected to become more prevalent during 1980 to 1985. These groups are waste oils, spent solvents, selected hazardous wastes listed in 40 CFR 261.31, and other high energy content organic waste materials being generated and currently disposed of at sites containing industrial boilers. Changes in the practice of boiler disposal for all groups will be influenced by recent and upcoming rules under RCRA. The three most pertinent RCRA related factors are the phase I (45FR33215) exclusion of burning a waste in an energy recovery process from subtitle C rules, phase II rules on incineration and possible future rules for boilers, and waste hauling and disposal costs or limitations as effected by the manifest and landfill rules.

Industries that are using an established disposal practice may change that practice because of changes in costs, onsite restrictions, new hauling requirements, or other factors. New requirements for onsite disposal as well as environmental controls on existing systems will increase the paperwork. Similar requirements for haulers and offsite disposal will increase costs to generators. These factors will be impacted by specific site costs that preclude projecting general trends in hazardous waste management.

Generators and haulers of hazardous wastes are anticipating changes in disposal practice because of significant upcoming rules. For example, if EPA extends the phase II requirement of 99.99-percent destruction from incinerators to include boilers as originally planned (Ref. 26), the practice of boiler destruction will certainly be affected. If the current boiler disposal exclusion is extended, then the conditions under which the exclusion is allowed will become very important.

Since EPA has funded other reviews of current waste management practices and the probable changes in practices that may occur, several findings of these efforts are presented. Other options for handling waste will directly compete with boiler disposal. Costs for competing optional management practices are covered in Table 10 while existing capacity of those options is presented in Table 11. Although capacity is apparently available for the

TABLE 10. REPORTED PRICES FOR HAZARDOUS WASTE MANAGEMENT SERVICES, 1980 (REF. 5)

Waste management option	Dollars per metric ton	Cents per gallon
Landfill[a]		
Wastes that are not acutely hazardous, including sludges	20-90	8-34
Highly toxic, explosives or reactives	100-400	38-152
Land treatment	5-25	2-9
Incineration		
High Btu value, no acute hazard	50-300	19-114
Highly toxic, heavy metals	300-1,000	114-378
Chemical treatment		
Acids, alkalines	15-80	6-30
Cyanides, heavy metals, highly toxic	100-500	38-200
Resource recovery	50-200	19-80
Deep-well injection		
Oily wastewaters	15-40	6-15
Dilute toxic rinse waters	50-100	19-38

[a] By comparison, disposal in sanitary landfills generally costs between $5 and $10 per ton.

TABLE 11. 1980 TOTAL CAPACITY FOR WASTE MANAGEMENT OPTIONS[5]

Waste management option	Capacity (thousand wet metric tons)	Current utilization (percent of capacity)
Land treatment/solar evaporation	2,437	22
Incineration	670	59
Chemical treatment[a]	3,921	54[b]
Resource recovery	1,069	40
Deep-well injection[c]	4,657	17
Subtotal	12,754	
Landfill (lifetime)	27,604	10.2 years
Total, all waste management options	40,358	

[a] Since there is an estimated 10-percent overlap between capacity to chemically treat and landfill material, the total capacity reported here represents capacity less overlap.

[b] Chemical treatment utilization computed on gross capacity of 4,357 wet metric tons.

[c] Although size of reservoir is many times larger, other factors such as unloading, incoming trucks, filtration and pumping dilution water may make it difficult to exceed 50 percent of the pumping rate according to facility operators. Capacity is based on 50 percent of pumping capacity or current utilization rate, whichever is highest.

NOTE

Accuracy of capacity estimates is judged to be ±25 percent.

near term, high costs of some options may suggest savings could be attained by changing disposal to boiler firing if this proves less expensive. (See Table 12 for 1980 to 1982 projected capacity.) A complete discussion of the way RCRA rules will impact various waste treatment options is presented in Reference 2.

3.3.1 Waste Oils

A large class of wastes that may increasingly be disposed in industrial boilers is waste oils -- emulsified, nonemulsified, or mixed. Contaminants are generally metals or organic liquids, but water, dirt, and other inert contaminants are common. As crude oil prices have increased over the past 8 years, the value of spent or contaminated oil has increased primarily because of its fuel value. Most of this oil is not re-refined for use as lubricants.

Several categories of waste oil have been increasingly reclaimed as a fuel additive. As stated earlier, re-refined oil sales volume decreased during the early 1970's and then slowly increased in the past 2 years. Competition came mainly from the fuel usage component of waste oil, which caused the unit price to increase rapidly (Ref. 15). This same factor is expected to decrease the amount of oil wasted directly to the environment and the waste from processing residual oily sludge. Essentially all oil disposed of onsite is currently burned or incinerated. Increased boiler disposal may occur for oils now lagooned, stored onsite, or land disposed. State inventory data (Ref. 9,11,23) and Harrison et al. (Ref. 1) indicate that only 20 to 45 percent of waste oil is currently disposed of onsite. Thus, the remaining oil wastes may be expected to constitute most of the heavily contaminated material available for burning. Impetus for destruction in boilers may increase disposal and displaced fuel as costs increase.

The conversion of oil disposal to boilers has been determined for two assumed rates, an increase of 10 and an increase of 40 percent over current levels, over the next 5 years. Such a conversion rate is applied only to the current disposal practices of lagooning, storage, landfilling, or incineration. An estimated 136 million liters are disposed of by incineration. The other disposal methods handle 371 million liters. Fifty-five percent of the additional waste oil generated in the future is assumed to be burned, a rate 10 percent higher than the current incidence of 45 percent. The anticipated growth of waste oil generation is projected to be 0.9 percent per year (Ref. 23). This translates to 433 million liters of additional generation in 1985. Fifty-five percent of this quantity is projected to be boiler disposed, or 238 million liters of this new waste oil. A summary of increased firing of waste oil (excluding oily sludge) for the assumed use rates is:

TABLE 12. HAZARDOUS WASTE MANAGEMENT INDUSTRY CAPACITY FORECASTS BY WASTE MANAGEMENT OPTION (1,000 WET METRIC TONS) (REF. 5)

Waste management option	1980			1981			1982		
	Lower bound	Baseline	Upper bound	Lower bound	Baseline	Upper bound	Lower bound	Baseline	Upper bound
Lifetime:									
Landfill[a]	20,979	27,604	34,229	23,048	30,334	37,619	19,094	25,124	31,157
Annual									
Land treatment	1,852	2,437	3,022	2,245	2,972	3,695	2,293	3,034	3,774
Incineration	509	670	831	779	1,037	1,295	1,094	1,490	1,886
Chemical treatment	2,980	3,921	4,862	3,546	4,787	6,028	4,450	5,910	7,370
Resource recovery	812	1,069	1,325	888	1,184	1,478	972	1,287	1,602
Deep-well injection	3,539	4,657	5,775	3,539	4,657	5,775	3,539	4,657	5,775

[a] Assumes regional utilization at 1980 rate or 5-year lifetime, whichever is highest, for 1981 and 1982 to determine lifetime capacity.

Oil source currently disposed	Increase use as fuel 1980 to 1985 (million liters)	
Incineration	13.6 10% to fuel	54.9 40% to fuel
Current disposal by means other than incineration or burning	37.1 55% to fuel	149.5 55% to fuel
Amount of increased new waste oil to fuel	238.1	238.1
Total	289.2	442.5
	(289,640 metric tons)	(443,180 metric tons)

An OSW study of the burning of waste oil in industrial boilers to be released in the near future may clarify the current practice of waste oil disposal.

3.3.2 Solvent Firing for Fuel

Increased firing of spent solvents is anticipated because of hazardous waste control regulations coupled with their generally high energy content and good firing characteristics (Ref. 1,14). Mixing of spent solvents with waste oils or oily material is common (Ref. 1). Since contradictions in the data on quantities of these wastes disposed by various means preclude a mass balance approach to estimate the extent of solvent firing, only specific solvent usage was reviewed.

Increases in firing solvents for fuel are projected as a result of increased onsite burning of waste solvents from increased solvent usage, increased burning of contaminated spent solvents previously landfilled and deep-well injected, and increased burning of solvent mixed with oily and organic liquid wastes. Boiler disposal of halogenated solvents or solvents currently incinerated is considered to remain negligible.

Currently, landfills, deep-well injection, and storage account for 212,730 metric tons per year of spent solvent disposal. This quantity was determined by multiplying the percent of spent solvents disposed of by these methods (24 percent (Ref. 1)) by the total quantity of spent solvents generated (875,000 metric tons) (Ref. 22,27). Solvent production is anticipated to increase at 1.2 percent per year, or by 57,270 metric tons over 5 years. A solvent content factor was determined from state inventory data (Ref. 9,10) for solvent in organic chemical still bottoms, liquids, and waste oils in the chemical industry. This factor (6.7 percent) times the SIC code 28 hazardous waste generation (25.5 million metric tons) gives 1.72 million metric tons. Currently 10 percent of this material, or 172,800 metric tons is disposed in boilers. If between a 10 and 40 percent increase in the incidence of this practice is probable, then an increase of 17,180 to 68,730 metric tons would be projected.

Solvent source	Increased use as fuel, 1980 to 1985 (metric tons per yr)	
	10% to fuel	40% to fuel
Currently directly disposed of in landfills, deep-well injection, or storage (now 212,730 metric tons per yr)	21,273	85,090
Increased production (at 1.2 percent per yr -- 57,270 metric tons)	5,727	22,910
Amount in still bottoms, liquids, or oils codisposed in boilers increase in practice	17,180	68,730
Total	44,180	176,730

3.2.3 Pulping Processes and Petroleum Refining

Quantities of petroleum refining waste firing and pulp manufacturing sulfite liquor firing are not anticipated to change between 1980 and 1985. Increases of petroleum refining production (<1 percent/yr) and the practice of refinery waste burning are considerably less than the inaccuracy of the original practice estimate of 7.6 million metric tons/yr. Production of pulping sulfite liquor is anticipated to decrease, although recovery and burning of other hazardous byproducts should increase slightly.

3.2.4 Miscellaneous Industries

To complete the quantification of the projected increase in the practice of boiler disposal of hazardous wastes, several SIC code industries were evaluated for significant possible increases not covered by oils or solvents. Two restrictions eliminated most industry segments. By limiting waste streams considered to those with high energy content, wastewater sludges and low organic content mixed wastes were excluded. The second limitation was to exclude all segments whose combustible waste was primarily waste oil or solvents, covered above. Excluded were the major combustible waste generating segments of SIC codes 26, 29, 30, 32, 34, 35, 37 and tentatively 22. Only segments covered by SIC codes 28 (organic chemicals) and 31 (leather products) appeared to have significant other combustible wastes. Food and kindred products (SIC code 20) was excluded since various background documents are contradictory, identifying the subject waste as either hazardous (Ref. 27) (290,000 metric tons/yr) or completely nonhazardous (Ref. 2). Some food processing waste is hazardous but is mainly composed of items not easily burned in boilers. These include pesticide residues in sludges, contaminated containers, and dyes. Hazardous organic materials used to process foods (i.e., coffee extracting) are disposed of in small quantities.

A detailed review of SIC codes 28 and 31 industries to determine the quantity of boiler disposable waste at facilities that have boilers would be quite time consuming. However, a short approach was followed for this report that was primarily based on previously compiled data (Ref. 5,14). For the chemical industry, the initial data included 14 million metric tons, wet weight, of hazardous wastes in SIC code 28 industries. The dry weight content was estimated to be 4.7 million metric tons. Of this material, 2.0 million metric tons was rated good or excellent for boiler disposal.[1] Based on usage, rather than waste generation, the solvent content of this waste (previously accounted for) amounts to 169,000 metric tons. The remaining 1.83 million metric tons is currently disposed of by other methods.

A factor was assigned to each current disposal technique which represented the probability that generators would discontinue disposal by the current process and burn the material in boilers instead. This factor is based on the premise that one or more of the following near-term pressures on the hazardous waste producer were likely to encourage such a change: savings in fuel, a change in existing equipment and systems, or a change in operating personnel and procedures. A current disposal method would be assigned a probability factor of 10 percent if it did not meet any of these criteria. 33 percent if it met one criterion, and 50 percent if it met two criteria.

Processes with minimal environmental impact to generators, hauling offsite to landfills or incineration, and controlled incineration were considered the processes least likely to change to boiler disposal, since no near-term pressures were likely to encourage this change. A 10 percent probability was assigned to these. Onsite deep-well and landfill disposal are more capacity-limited and expensive to operate. A factor of 33 percent was assigned here since only one of the three factors favor it. Uncontrolled incineration is expected to face some plant changes because of the phase II requirements; thus, a full 50 percent would be expected to change disposal to boiler feed due to economy.

Process	Percent waste treated (Ref. 14)	Probability factor for disposal change
Landfill	14.8	0.33
Deep well	2.0	0.33
Uncontrolled incineration	48	0.5
Controlled incineration	21.6	0.1
Landfill offsite	3.6	0.1
Incineration offsite	1.5	0.1
Weighted average	--	0.32

By applying the composite conversion (from other disposal to boilers) probability factor for organic chemical hazardous wastes (0.32) to the quantity of nonsolvent hazardous wastes identified (Ref. 27) (3.31 million metric tons after adjustment to include all the current nonsolvent total SIC code 28 hazardous wastes), a total of 1.06 million metric tons is obtained. New production of waste is projected to be 4.3 percent per year (same as industry growth) and amounts to 704,500 metric tons by 1985.

Using the increased boiler disposal fractions of 10 and 40 percent, the annual amounts are:

Source	Increased use as fuel, 1980 to 1985 (metric tons per yr)	
Organic chemicals (nonsolvent SIC code 28)	10%	40%
Conversion from other disposal	96,360	385,440
New production	70,450	281,800
Total	166,810	667,240

The leather finishing and tanning industry (SIC code 31) has been assessed for hazardous wastes in several studies. Currently, EPA is changing the listing of all chromium as a major toxicant and substituting only hexavalent chromium. Also, some tanning wastes were removed from the list (November 1980). Only an estimated 5 percent of the existing tanneries have coal or other solid fuel boilers that could fire their hazardous waste solids. Furthermore, the quantity of hazardous wastes by definition for this industry has decreased by over half by the chromium component clarification -- down to 218,000 metric tons (Ref. 5). Future growth is not expected for this industry. Using 10 and 40 percent waste disposal fractions and the prior factors, the annual amounts are:

Source	Increased use as fuel, 1980 to 1985 (metric tons per yr)	
	10%	40%
Leather tanning and finishing (SIC code 31)	1,100	4,400

3.2.5 Evaluation of Quantification Approach

The approach presented above appears more reasonable than using a purely SIC code summary approach, as the latter requires better composite data than are available. An example has been selected to illustrate this point.

Supporting data for EPA's Environmental Impact Statement (April 1980) contained an estimated value of 2.87 million metric tons for SIC code 26 industries without identification of its composition. EPA's background document on Hazardous Waste Generation (Ref. 5) identified SIC code 26 as having 1.22 million metric tons/yr of total hazardous waste. No wastes were included on the "EPA Waste List" or as "characteristic wastes." It was further estimated that the range of values was 0 to 1.76 million metric tons and was generally composed of wastewater treatment sludges with onsite disposal (97 percent) in lagoons. However, among the itemized hazardous wastes inventoried by states, the following materials were listed:

- Halogenated solvents
- Nonhalogenated solvents
- Unknown solvents
- Mixture of solvents
- Other organic liquids
- Ink solids and sludges
- Metal finishing sludge
- Paper sludge
- Nonemulsified waste oil
- Lab chemicals

- Nonhalogenated tank residue
- Textile coating solutions
- Rinse water and wastewaters
- Other mixed waste

This list indicates that solvents and waste oil do compose a part of SIC code 26 waste, about 60 percent by weight, though these categories are not specifically called out in EPA's waste generation inventory.

For one state, the inventoried waste was two-third's organic and the remainder inert or metallic. On the other hand, wastewater sludges, estimated at approximately 1.6 million metric tons/yr (based on 1980 projected production of 62 million tons) are rarely hazardous and not included in most inventories. (These wastes are usually landfilled onsite after several years storage or sent to publicly owned treatment works. A small quantity of material is reclaimed and some burned both for fuel and simply incinerated for consolidation.) Thus, if the EPA waste generation data base and categories were used, no hazardous wastes would be listed as possible boiler disposed. However, by alternatively selecting waste oils and solvents, specifically called out in some state inventories, considerable material would be listed as candidates for such a practice.

Similar difficulties would be encountered if EPA generator values were selected for SIC code 32. Here the EPA data base (Ref. 5) specifically tabulates solvents and acid waste. However, the total quantity of hazardous waste estimated here is lower than the quantity of solvents listed in state inventories (Ref. 9,10,24).

SIC code 28 state inventories likewise exceed the EPA generator values due principally to the contribution of spent solvents. Thus, the selection of generic materials (oil and solvent) provided a better base for projecting waste burning practices than would have been accomplished using types of industry data.

3.2.6 Summary of Waste Quantities

The quantity of hazardous wastes that is projected to be disposed in boilers is summarized as follows:

Source	Increased use as fuel, 1980-1985 (metric tons per yr)	
	10%	40%
Waste oils	289,640	443,180
Solvents	44,180	176,730
Organic chemicals	166,810	667,240
Tanning	1,100	4,400
Total	501,730	1,291,550

If only 10 percent of the wastes identified as likely candidates for boiler disposed materials are so disposed, it will amount to an increase in half a million metric tons/yr additional boiler disposal in 1985 over current levels of about 18.8 million metric tons. If 40 percent of these wastes become boiler disposed, a projected additional 1.3 million metric tons will be boiler disposed.

SECTION 4

INDUSTRIAL BOILER POPULATION

This section establishes the industrial boiler population inventory required to support the technical overview of hazardous waste disposal in industrial boilers. The objectives were twofold. The first was to assemble an inventory of the industrial boiler population, specifically broken down by capacity, design type, fuel fired, and regional location. This inventory could then be combined with the regional inventory of hazardous waste generation described in Section 3 to provide what might be termed the "matrix of opportunity" for hazardous waste combustion in industrial boilers.

The second objective was to select and describe the characteristics of a set of standard boilers representative of those most widely used by industry. These descriptions include specifying the capacity, design type, and fuel fired so that the standard boilers would be representative of installed capacity.

4.1 INDUSTRIAL BOILER INVENTORY

In assembling this inventory, attention was focused solely on industrial boilers with heat input capacities greater than 2.9 MW (10 million Btu/hr). Commercial and institutional boilers were not included since these establishments generate negligible quantities of hazardous waste. The capacity limitation is applied since smaller units are generally natural-gas-or oil-fired firetube, or cast iron units used for space heating. Such units do not easily lend themselves to either waste firing or to the fuel blending required in waste cofiring.

Establishing an industrial boiler population inventory is complicated by several factors:

- Virtually all industries in the U.S. use boilers for space heat and process steam
- Industrial boilers are sold by a large number of manufacturers, almost all of which consider their sales data proprietary
- Unit retirement rates are unknown; many units have been in operation well over 50 years
- Identifying the fuel fired is difficult because (1) many units were sold to fire several fuels, and (2) many other units that were sold to fire a single fuel have since been modified to fire another

Perhaps the most comprehensive and well-documented attempt to establish an industrial boiler inventory was performed by Battelle (Ref. 28,19). This 1971 population inventory has long been regarded as the best available. A more recent characterization of the industrial boiler population has been assembled by PEDCo (Ref. 30). The PEDCo effort essentially used Battelle's work as a baseline, and updated the 1971 inventory to 1977 using sales data from the American Boiler Manufacturers Association (ABMA) and the Hydronics Institute. Most of the data presented in this section were derived from PEDCo's effort.

As noted in the introduction to this section, the desired boiler inventory characterizes the installed population by capacity, design type, fuel, and regional location. The PEDCo 1977 inventory provides information with respect to the first three, but has no regional breakdown. To provide the desired regional data, results of another PEDCo study were used (Ref. 31). This second study compiled National Emission Data System (NEDS) information on industrial boilers and gives a state-by-state breakdown of units reported in the NEDS base.

Unfortunately, the NEDS-based information accounts for only about 16,000 industrial boilers with capacity greater than 2.9 MW (10 million Btu/hr). The aggregate capacity of these units comprises 530 GW (1.8 x 10^{12} Btu/hr). In contrast, the national inventory contains about 43,000 units and 730 GW (2.5 x 10^{12} Btu/hr) of capacity (Ref. 30). In addition, the NEDS-based data do not provide a design type breakdown. The fuel type categories also differ. For example, the NEDS-based data includes process gas; the national inventory does not. Finally, the size range categories differ; the NEDS-based data has only two size ranges, 2.9 to 29 MW (10 to 100 million Btu/hr) and greater than 29 MW (100 million Btu/hr), whereas the national inventory has seven size ranges.

To prepare the boiler inventory by region and capacity and adjust the NEDS information to approximate the national inventory, the two data systems were combined using the following guidelines:

- The national inventory was reorganized by design type, capacity, and fuel categories as used in the NEDS-based inventory
- The reorganized inventory was distributed among the states (both number of units and capacity) according to the fractional distribution (by capacity and fuel) as defined by the NEDS-based inventory
- Each state's inventory was distributed between design type according to the national fractional distribution
- This state-by-state inventory was combined into an EPA regional inventory (both number of units and capacity)

It should be emphasized that this approach gives only an approximation to an actual regional inventory because of its underlying assumptions. The most critical assumptions implicit in this approach are:

- The NEDS-based inventory gives an accurate representation of the statewide fractional distribution of units and capacity, by capacity range and fuel. This implies that the NEDS undercounting (compared to the national inventory) of units and capacity does not vary state to state.
- The design type distribution of boilers does not vary state by state and can be represented by the national inventory

Neither of these assumptions is absolute. Therefore, the regional characterization obtained in this manner must be considered to be an approximation.

Tables 13 and 14 present the results of this regional industrial boiler population characterization. Table 13 categorizes units in the 2.9 to 29 MW (10 to 100 million Btu/hr) heat input capacity range. Table 14 gives a corresponding breakdown for units with capacities greater than 29 MW (100 million Btu/hr). Table 15 presents a summary of regional population by capacity only.

4.2 TYPICAL BOILERS

To establish if industrial boilers are appropriate for the disposal of hazardous wastes, the combustion characteristics of industrial boilers in terms of their temperature-time profiles must be defined. The temperature-time profile of a boiler depends on several variables, most notably design type, capacity, operating load, and fuel fired. Therefore, to define industrial boiler combustion characteristics, a set of "typical" units was defined to represent the key features of the nation's boiler population.

Selecting the set of typical boilers to be characterized in this study was guided by work done by PEDCo and documented in the national boiler population inventory study (Ref. 30). The set of typical boilers selected as representative of the installed population by fuel and design type is given in Table 16.

The 4.4-MW firetube boiler firing either natural gas or distillate oil represents a larger than average firetube unit but is typical of the capacity range of interest in this study. The 44-MW packaged watertube units firing residual oil, distillate oil, or natural gas represent typical large industrial boilers firing liquid or gas fuels. The 44-MW spreader-stoker-fired watertube unit is typical of larger stokers currently being sold. The 59-MW pulverized-coal unit is representative of industrial pulverized-coal units, though it is on the lower capacity range of a typical pulverized-coal unit, most of which are used for utility electricity generation. This set of typical boilers spans the range of equipment found in the industrial steam-generating sector.

Utilizing the data from Section 3 on the number of waste generators and Section 4 on the boiler inventory, Table 17 can be generated. If the compounds from class B (Section 3) are used as supplemental fuel, an analysis of the availability of boiler capacity to consume the waste can be conducted.

TABLE 13. REGIONAL DISTRIBUTION OF U.S. INDUSTRIAL BOILERS IN THE 2.9 TO 29 MW CAPACITY RANGE (MW (MILLION BTU/HR))

EPA region		Watertube boilers							Firetube boilers					
		Spreader stoker	Underfeed stoker	Overfeed stoker	Residual oil	Distillate oil	Natural gas	Process gas	Coal	Residual oil	Distillate oil	Natural gas	Process gas	Total
I	Number of units	5	14	2	1,253	22	106	--	7	747	45	102	--	2,303
	Capacity	51 (174)	148 (505)	22 (75)	11,262 (38,430)	168 (573)	1,513 (5,163)	-- (--)	38 (130)	3,474 (11,850)	211 (720)	631 (2,150)	-- (--)	17,518 (59,770)
II	Number of units	2	8	2	1,344	98	314	--	4	803	206	299	--	3,080
	Capacity	7 (24)	24 (82)	6 (20)	17,021 (58,081)	981 (3,350)	4,945 (16,870)	-- (--)	12 (41)	5,250 (17,910)	1,240 (4,231)	2,062 (7,036)	-- (--)	31,548 (107,650)
III	Number of units	141	432	104	1,131	145	572	20	232	674	306	546	20	4,323
	Capacity	2,264 (7,725)	6,548 (22,340)	1,659 (5,661)	15,215 (51,918)	1,736 (5,924)	8,399 (28,660)	298 (1017)	1,628 (5,555)	4,692 (16,010)	2,185 (7,456)	3,503 (11,950)	125 (427)	48,252 (164,650)
IV	Number of units	169	517	126	1,455	413	2,614	50	276	868	870	2,499	48	9,905
	Capacity	1,907 (6,507)	5,526 (18,860)	1,396 (4,764)	14,897 (50,833)	3,931 (13,410)	30,257 (103,250)	989 (3,375)	1,370 (4,675)	4,595 (15,680)	4,910 (16,750)	15,287 (52,164)	421 (1,437)	85,486 (291,710)
V	Number of units	407	1,241	302	940	210	1,642	153	666	561	452	1,564	145	8,283
	Capacity	6,254 (21,340)	18,137 (61,889)	4,621 (15,770)	13,387 (45,681)	2,998 (10,230)	24,029 (81,995)	2,429 (8,289)	4,480 (15,290)	4,130 (14,090)	3,473 (11,850)	11,540 (39,378)	1,013 (3,537)	96,491 (329,260)
VI	Number of units	1	2	--	37	26	1,241	99	1	23	51	1,182	96	2,759
	Capacity	4 (14)	11 (38)	-- (--)	461 (1,573)	335 (1,143)	15,816 (53,969)	1,593 (5,436)	4 (14)	143 (488)	423 (1,443)	6,619 (22,590)	672 (2,293)	26,081 (89,000)
VII	Number of units	16	50	12	288	155	1,228	10	26	137	327	1,170	10	3,369
	Capacity	263 (897)	763 (2,604)	183 (624)	2,676 (9,131)	1,158 (3,951)	10,664 (36,389)	145 (495)	191 (652)	825 (2,815)	1,453 (4,958)	5,156 (17,590)	60 (205)	23,537 (80,310)
VIII	Number of units	4	10	1	109	17	222	44	5	66	34	212	42	766
	Capacity	38 (130)	109 (372)	12 (41)	1,687 (5,757)	146 498	3,013 (10,280)	734 (2,505)	29 (99)	521 (1,778)	184 (628)	1,257 (4,289)	306 (1,044)	8,036 (27,420)
IX	Number of units	--	--	--	673	131	573	12	--	402	278	522	12	2,603
	Capacity	-- (--)	-- (--)	-- (--)	5,296 (18,070)	467 (1,594)	3,616 (12,340)	144 (491)	-- (--)	1,635 (5,579)	869 (2,965)	2,217 (7,565)	60 (205)	14,304 (48,810)
X	Number of units	4	14	3	121	41	146	2	7	72	84	140	2	636
	Capacity	37 (126)	104 (355)	26 (89)	1,928 (6,579)	655 (2,235)	2,850 (9,725)	51 (174)	28 (96)	595 (2,030)	822 (2,805)	1,190 (4,061)	21 (72)	8,307 (28,350)
Total	Number of units	749	2,288	552	7,291	1,258	8,658	390	1,224	4,353	2,653	8,236	375	38,027
	Capacity	10,825 (36,940)	31,370 (107,050)	7,925 (27,040)	83,830 (286,060)	12,575 (42,910)	105,102 (358,330)	6,383 (21,780)	7,780 (26,550)	25,860 (88,240)	15,770 (53,810)	49,462 (168,780)	2,678 (9,140)	359,560 (1,226,930)

TABLE 14. REGIONAL DISTRIBUTION OF U.S. INDUSTRIAL BOILERS WITH CAPACITY GREATER THAN 29 MW (MW (MILLION BTU/HR))

EPA region		Watertube boilers[a]								
		Pulverized coal	Spreader stoker	Underfeed stoker	Overfeed stoker	Residual oil	Distillate oil	Natural gas	Process gas	Total
I	Number of units	1	2	--	--	172	--	18	--	193
	Capacity	62 (212)	184 (628)	-- (--)	-- (--)	8,749 (29,850)	-- (--)	1,217 (4,153)	-- (--)	10,212 (34,850)
II	Number of units	52	15	6	3	183	5	35	3	302
	Capacity	3,727 (12,720)	2,751 (9,387)	1,082 (3,692)	621 (2,119)	9,661 (32,970)	309 (1,054)	17,286 (58,990)	131 (447)	35,568 (121,370)
III	Number of units	167	60	23	12	171	18	86	50	587
	Capacity	12,763 (43,550)	4,030 (13,750)	1,584 (5,405)	911 (3,109)	10,383 (35,430)	877 (2,976)	3,936 (13,430)	4,647 (15,860)	39,126 (133,510)
IV	Number of units	160	106	38	22	332	37	331	27	1,053
	Capacity	12,643 (43,140)	6,887 (23,500)	2,708 (9,241)	1,552 (5,296)	22,768 (77,690)	1,746 (5,958)	20,271 (69,170)	1,282 (4,375)	69,857 (238,380)
V	Number of units	278	321	124	64	242	48	430	20	1,527
	Capacity	23,909 (81,590)	13,605 (46,420)	5,617 (19,170)	3,224 (11,000)	17,132 (58,460)	2,316 (7,903)	23,040 (78,620)	3,337 (11,390)	92,180 (314,550)
VI	Number of units	--	--	--	--	57	43	481	90	671
	Capacity	-- (--)	-- (--)	-- (--)	-- (--)	7,349 (25,080)	3,055 (10,420)	56,889 (154,120)	10,997 (37,530)	78,290 (267,150)
VII	Number of units	32	31	11	7	38	18	104	11	252
	Capacity	1,824 (6,224)	1,730 (5,903)	680 (2,320)	389 (1,327)	2,060 (7,029)	705 (2,406)	4,974 (16,970)	662 (2,260)	13,024 (44,440)
VIII	Number of units	15	11	3	2	22	5	97	12	117
	Capacity	4,072 (13,890)	834 (2,846)	134 (457)	77 (263)	1,077 (3,675)	318 (1,085)	2,453 (8,370)	770 (2,627)	9,735 (33,220)
IX	Number of units	--	3	1	1	79	17	60	22	183
	Capacity	-- (--)	225 (768)	89 (304)	51 (174)	5,084 (17,350)	733 (2,500)	3,596 (12,270)	996 (3,399)	10,774 (36,760)
X	Number of units	14	13	4	2	68	9	97	3	160
	Capacity	1,075 (3,668)	1,059 (3,614)	416 (1,420)	240 (819)	3,897 (13,300)	401 (1,368)	2,717 (9,271)	254 (867)	10,059 (34,320)
Total	Number of units	719	562	210	113	1,364	200	1,639	238	5,045
	Capacity	60,075 (205,000)	31,305 (106,820)	12,310 (42,000)	7,065 (24,110)	88,160 (300,830)	10,455 (35,680)	136,379 (465,370)	23,076 (78,740)	368,825 (1,258,550)

[a] No firetube boilers have capacities greater than 29 MW

TABLE 15. REGIONAL DISTRIBUTION OF U.S. INDUSTRIAL BOILERS WITH CAPACITY GREATER THAN 2.9 MW (MW (MILLIION BTU/HR)

Capacity range[a]		EPA Region										Total
		I	II	III	IV	V	VI	VII	VIII	IX	X	
2.9-29 (10-100)	Number of units	2,303	3,080	4,323	9,905	8,283	2,759	3,369	766	2,603	636	38,027
	Capacity	17,518 (59,770)	31,548 (107,650)	48,252 (164,650)	85,486 (291,710)	96,491 (329,260)	26,081 (89,000)	23,537 (80,310)	8,036 (27,420)	14,304 (48,810)	8,307 (28,350)	359,560 (1,226,930)
>29 (>100)	Number of units	193	302	587	1,053	1,527	671	252	117	183	160	5,045
	Capacity	10,212 (34,850)	35,568 (121,370)	39,126 (133,510)	69,857 (238,380)	92,180 (314,550)	78,290 (267,150)	13,024 (44,440)	9,735 (33,220)	10,774 (36,760)	10,059 (34,320)	368,825 (1,258,550)
Total	Number of units	2,496	3,382	4,910	10,958	9,810	3,430	3,621	833	2,786	796	43,072
	Capacity	27,730 (94,620)	67,116 (229,020)	87,378 (298,160)	155,343 (530,090)	188,671 (643,810)	104,371 (356,150)	36,561 (124,750)	17,771 (60,640)	25,078 (85,570)	18,366 (62,670)	728,385 (2,485,480)

[a] Thermal input

TABLE 16. TYPICAL INDUSTRIAL BOILERS

Heat input capacity (MW (million Btu/hr))	Fuel	Design type
4.4 (15)	Distillate oil	Packaged -- scotch firetube
4.4 (15)	Natural gas	Packaged -- scotch firetube
44 (150)	Residual oil	Packaged -- watertube
44 (150)	Distillate oil	Packaged -- watertube
44 (150)	Natural gas	Packaged -- watertube
44 (150)	Stoker coal	Field-erected -- spreader stoker -- watertube
59 (200)	Pulverized coal	Field-erected -- watertube

TABLE 17. GEOGRAPHIC DISTRIBUTION OF BOILERS AND WASTE GENERATORS

	EPA Region										
	I	II	III	IV	V	VI	VII	VIII	IX	X	Total
Number of boilers 2.9-29 MW (10-100 x million Btu/hr)	2,303	3,080	4,323	9,905	8,283	2,759	3,369	766	2,603	636	38,027
Number of boilers >29 MW (>100 x million Btu/hr)	193	302	587	1,053	1,527	671	252	117	183	160	5,045
Total boilers	2,496	3,382	4,910	10,958	9,810	3,430	3,621	833	2,786	796	43,072
Number of Waste Generators	3,370	5,260	5,080	6,920	9,800	8,270	2,270	1,570	4,315	1,500	48,355

Total industrial boiler population (including size <10 x million Btu/hr) 238,000

By making certain assumptions, the boiler capacity available to destroy class B hazardous wastes can be approximated. There are 43,000 boilers with aggregate capacity of 728 GW (2.5 x 10^{12} Btu/hr), for an average boiler size of 17 MW (58 x million Btu/hr). The assumptions necessary for this evaluation are

- 10 percent of the total available boiler capacity will be selected for utilization to destroy hazardous waste
- The hazardous wastes will represent 5 percent of the total Btu input to the boiler
- Combustion of these hazardous wastes yield approximately 33 MJ/l (120,000 Btu/gal) and the hazardous wastes have an average density of 0.95 kg/l
- Boilers will operate 300 days/year and 24 hours/day

Using the class B hazardous waste quantities generated, the calculated maximum waste quantity destructible (as limited by these assumptions) is shown in Table 18. Though each region may not have sufficient boiler capacity to consume all class B waste, it is projected that sufficient boiler capacity exists to destroy significant quantities.

TABLE 18. GEOGRAPHIC DISTRIBUTION OF CLASS B HAZARDOUS WASTE DESTRUCTION CAPACITY (1,000 METRIC TONS/HR)

	EPA Region										
	I	II	III	IV	V	VI	VII	VIII	IX	X	Total
Combustible constituents (class B) generation	19	109	173	535	176	570	45	7	112	19	1,765
Quantity of hazardous waste destructible	87	118	172	384	343	120	127	29	97	28	1,508

SECTION 5

CHARACTERIZATION OF INDUSTRIAL BOILERS

The efficient destruction of combustible hazardous waste achievable in industrial boilers is primarily dependent on the temperature and residence time profiles of the combustion products as they pass through the furnace. The destruction efficiency of any species is maximized when the gas temperature and residence time are maximized. Since industrial boilers are nonadiabatic reactors, the temperature of the combustion products peaks in the flame zone and is reduced as heat is absorbed by the furnace walls. Thus, a representative temperature-time profile through the combustion zone is necessary to estimate the destruction potential for hazardous waste constituents.

This section presents design and operating characteristics of typical industrial boiler types and estimates bulk gas temperatures and residence time profiles in the combustion chamber of these boilers. The temperature and residence times necessary to reach the required destruction efficiencies are coupled with selected hazardous waste characteristics in Section 6. As a prelude to the determination that destruction of a hazardous waste in a boiler represents a viable disposal option, the physical compatability between the boiler and proposed waste must be carefully evaluated. This evaluation is primarily concerned with the mechanical changes required to allow firing of the waste. This includes facility design, retrofit considerations, fuel requirements, burner considerations, and process feasibility. Section 5.3 discusses the key elements for this evaluation.

5.1 DESCRIPTION OF BOILERS, FUELS, AND OPERATING CHARACTERISTICS

The temperature-time profile of combustion gases in boiler furnaces varies with boiler design and operating characteristics such as furnace geometry, burner configuration, fuel type, heat input, and excess air level. As presented in Section 4, seven individual boiler design/fuel combinations were selected for consideration in this study. The following discussion summarizes the design and operating factors for each boiler/fuel combination.

Table 19 lists the boiler design types, the heat input capacities, and the ultimate analyses of fuel assumed. Table 20 summarizes furnace dimensions and fuel and combustion air flowrates and temperatures for each unit. Furnace dimensions were obtained in part from published design data (Ref. 32,33) and from telephone contacts with major boiler manufacturers

TABLE 19. MODEL INDUSTRIAL BOILERS AND FUELS USED IN THE ANALYSIS

Assigned identification	Boiler	Capacity MW (million Btu/hr)	Fuel							Fuel higher heating value (MJ/kg (Btu/lb))	Typical operating load factor (% capacity)
			Type	% C	% H_2	% S	% O_2	% Ash	% H_2O .		
A	Packaged scotch firetube	4.4 (15)	Distillate oil	87.2	12.5	0.3	Nil	--	--	42.6 (18,300)	45
B	Packaged scotch firetube	4.4 (15)	Natural gas	74.7	12.5	--	--	--	--	53.3 (22,900)	45
C	Packaged watertube	44 (150)	Residual oil	86	11.0	3.0	0.3	0.05	--	42.3 (18,200)	55
D	Packaged watertube	44 (150)	Distillate oil	87.2	12.5	0.3	Nil	--	--	42.6 (18,300)	55
E	Packaged watertube	44 (150)	Natural gas	74.7	23.3	--	--	--	--	53.3 (22,900)	55
F	Field erected watertube spreader stoker	44 (150)	Bituminous coal[a]	72.8	4.8	2.2	6.2	9.0	3.5	30.4 (13,080)	60
G	Field erected watertube pulverized coal	58.6 (200)	Bituminous coal[a]	72.8	4.8	2.2	6.2	9.0	3.5	30.4 (13,080)	60

[a] ASTM Rank: Class II Group 3.
Ash fushion temperature -- 1,511K (2,260°F) at initial deformation.

TABLE 20. DESIGN AND OPERATING CHARACTERISTICS OF MODEL BOILERS

Assigned identi-fication	Boiler	No. of burners or feeders	Approximate furnace dimensions (m (ft)) Length	Width	Height	Furnace heating surface (m^2 (ft^2))	Furnace volume (m^3 (ft^3))	Fuel flow (kg/s (lb/hr))	(kg/s (10^3 lb/hr))	temperature (°K (°F))	temperature (°K (°F))	Excess O_2 in furnace (%)	Flue gas mass flow (kg/s (10^3 lb/hr))	Flue gas volumetric flow (m^3/s (scfm))	Other boiler descriptions
A	Packaged scotch firetube	1	4.6 (15)	0.76 D[a] (2.5 D)		11 (118)	2.1 (74)	0.10 (820)	1.71 (13.6)	300 (80)	300 (80)	3.0	1.83 (14.5)	1.35 (2,860)	Dryback, three pass
B	Packaged scotch firetube	1	4.6 (15)	0.76 D (2.5 D)		11 (118)	2.1 (74)	0.08 (655)	1.59 (12.6)	300 (80)	300 (80)	3.0	1.66 (13.2)	1.18 (2,490)	Dryback, three pass
C	Packaged watertube	1	11.9 (39)	2.0 (6.5)	2.7 (9)	117 (1,260)	68 (2,400)	0.96 (1,580)	15.3 (121)	355 (180)	450 (350)	3.0	16.3 (129)	13.2 (28,000)	D-type, refractory base
D	Packaged watertube	1	11.9 (39)	2.0 (6.5)	2.7 (9)	117 (1,260)	68 (2,400)	0.95 (7,540)	15.8 (125)	300 (80)	450 (350)	3.0	16.6 (132)	13.2 (28,000)	D-type, efractory base
E	Packaged watertube	1	11.9 (39)	2.0 (6.5)	2.7 (9)	117 (1,260)	68 (2,400)	0.77 (6,120)	15.0 (119)	300 (80)	450 (350)	1.0	15.8 (125)	11.8 (24,900)	D-type, refractory base
F	Field erected watertube spreader stoker	4	5.2 (17)	4.3 (14)	9.8 (32)	155 (1,670)	212 (7,500)	1.35 (10,700)	18.5 (147)	300 (80)	450 (350)	6.0	19.9 (158)	14.7 (31,100)	Effective grate area = 20 m^2 (215 ft^2)
G	Field erected watertube pulverized coal	4	5.5 (18)	5.2 (17)	15.8[b] (52)	286 (3,080)	317 (11,200)	1.78 (14,140)	23.3 (185)	339 (150)	477 (400)	5.0	25.2 (200)	18.2 (38,500)	Single wall, dry bottom

[a] D -- diameter.

[b] Total furnace height from bottom hopper to convective section.
Height above main burner zone is 7.9m (26 ft) for a combustion volume of 107 m^3 (3,800 ft^3) assuming horizontal firing.

(Ref. 34-37). Although furnace dimensions reported here are typical of these boiler designs, they are not to be considered specific to any industrial boiler manufacturer.

The furnace gas exit temperature is a vital design consideration. A furnace exit temperature of 1,300K (1,880°F) indicates that about one half of the heat released by the fuel is absorbed by the furnace walls prior to the combustion gas entering the convective region of the boiler. In the case of coal combustion, the design flue gas temperature at the exit of the furnace is heavily dependent on coal rank and its ash properties. For example, the design exit temperature at full load is normally 110K (200°F) less than the fusion temperature of the ash in the coal. This design criterion is imposed to minimize fouling of the convective passes by deposition of molten coal ash on the heat transfer tubes. This design exit temperature, together with coal combustion characteristics, determines the overall size of the furnace and, thus, the bulk residence time of the combustion products. Gas exit temperature was also verified through contacts with boiler manufacturers (Ref. 34-37).

Table 21 summarizes the estimated peak temperatures in the primary combustion zone and design flue gas exit temperatures at full load operation. Based on the high and low gas temperatures, the bulk gas residence time and heat absorbed in the furnace were calculated. These values are refined in Section 5.3 with the application of a mathematical model to calculate temperature profiles.

5.2 TEMPERATURE-TIME PROFILE CALCULATIONS

At the onset of this task, a review of published boiler literature was conducted to compile empirical temperature and heat transfer data throughout industrial boiler furnaces. This literature consisted mainly of technical brochures from industrial boiler manufacturers and field test reports performed under numerous domestic and foreign government-sponsored environmental and boiler performance studies. This review showed the near absence of pertinent data. Further telephone contacts with major industrial boiler manufacturers indicated that although empirical data and predictive mathematical schemes to estimate the temperature profile were available from selected manufacturers, this information was considered proprietary or not easily available within the timeframe of this study. Technical information released by boiler manufacturers consisted of typical furnace dimensions and approximate exit temperatures as indicated in Section 5.1.

Therefore, to estimate temperature-time profiles, it was necessary to devise a computational scheme based on proven techniques and thermodynamic relationships. The following discussion describes one such scheme used to calculate temperature-residence time profiles of the combustion products throughout the radiant section of each industrial boiler described in Section 5.1. Limitations of the model and assumptions used are also discussed.

TABLE 21. CALCULATED RESIDENCE TIMES AND FURNACE TEMPERATURES

Assigned boiler identification	Fuel	Percent of operating capacity	Total heat input (MW million Btu/hr))	Furnace heat release rate (kW/m^2 (million Btu/hr-ft^2))	Furnace heat liberation rate (kW/m^3 (10^3 Btu/hr-ft^3)	Average flame or bed temperature in active combustion zone (°K (°F))	Average furnace residence time (s)	Furnace exit temperature (°K (°F))	Heat adsorbed in the furnace (MW (million Btu/hr))
A	Distillate oil	100	4.4 (15.0)	400 (127)	2,100 (203)	2,144 (3,400)	0.22	1,589 (2,400)	1.52 (5.2)
B	Natural gas	100	4.4 (15.0)	400 (127)	2,100 (203)	2,255 (3,600)	0.23	1,589 (2,400)	1.17 (5.7)
C	Residual oil	100	44.0 (150)	375 (119)	652 (63)	2,255 (3,600)	0.79	1,283 (1,850)	25.1 (85.8)
D	Distillate oil	100	44.0 (150)	375 (119)	652 (63)	2,200 (3,500)	0.77	1,366 (2,000)	24.4 (83.2)
E	Natural gas	100	44.0 (150)	375 (119)	652 (63)	2,283 (3,650)	0.82	1,477 (2,200)	23.7 (81.0)
F	Bituminous coal	100	44.0 (150)	287 (91)	207 (20)	1,722 (3,000)	1.90	1,400 (2,060)	16.9 (57.6)
G	Bituminous coal	100	59.2 (202)	208 (66)	186 (18)	2,060 (3,250)	1.82	1,400 (2,060)	25.3 (86.3)

5.2.1 Mathematical Model

One of the more complete and widely used mathematical models of radiation heat transfer in turbulent diffusion flames is the zone method of analysis (Ref. 38). In this model, the furnace of a given boiler is divided into a number of zones for which steady-state energy balances are developed. This procedure assumes that the zones are small enough to be isothermal and that the flue gas properties within the zone are constant. Thus, the larger the number of zones, the more precise the profile. The simultaneous solution of the energy balance equations for all zones leads to the temperature distribution in the furnace and, consequently, the evaluation of the heat flux in the furnace.

An underlying assumption in this approach is that the gas in the furnace is perfectly mixed in radial or lateral directions. This assumption, though not conservative, generally introduces small uncertainties in model predictions.

Since the model assumes that a given zone is isothermal, each zone is represented by a single effective radiating temperature. In reality, the gas temperature varies at any one cross section in the furnace, as illustrated in Figure 1. The gas temperature near the furnace walls can be significantly less than the mean radiating temperature, by about 100°K (180°F). This aspect of temperature distribution across a given zone was considered when estimating the destruction efficiency of hazardous wastes injected into the furnace.

The thermal zone model (Ref. 38) has been shown to be suitable for both nonluminous flames (those from natural gas combustion) having low emissivities as well as luminous flames (those from oil and coal combustion) having high emissivities. The presence of suspended soot and carbon particles in a hot gas gives the flame its luminous characteristics and contributes to its high radiating property.

5.2.1.1 Energy Balance and Temperature Calculations

A computational routine based on a steady-state energy balance within each zone was devised in order to calculate the gas temperature profile throughout the furnace and evaluate the heat flux characteristics. With the aid of the computer, the energy balance calculations were performed simultaneously for each isothermal zone in the furnace until a gas temperature profile consistent with known radiative and convective heat fluxes was obtained. This section briefly discusses the energy balance computational scheme used for the temperature profile calculations and presents the primary assumptions and limitations of the model as it was used in this study.

Figure 2 shows a plan view schematic of a packaged, single burner, watertube boiler (44 MW, 150 million Btu/hr), representing boiler type D in Tables 19 through 21. As illustrated, the furnace has been divided into six equal cubical zones. The shape of the zone is dictated by the geometry of

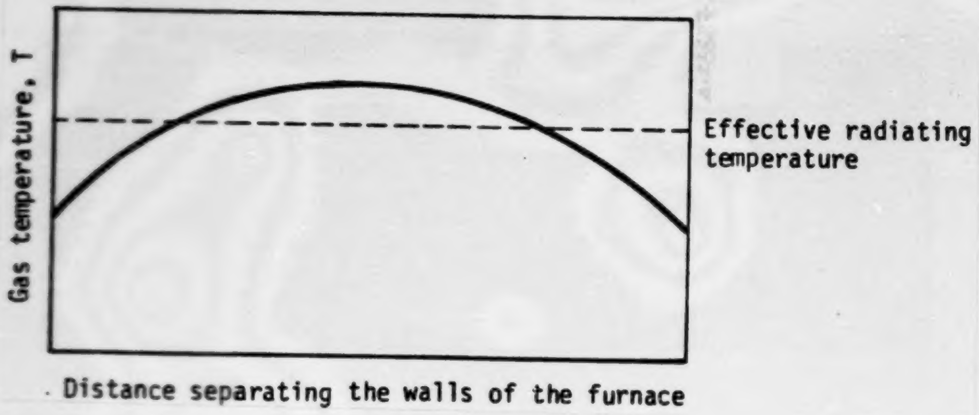

Figure 1. Temperature distribution across a heat generating and absorbing medium contained between furnace walls (Ref. 39).

the furnace, and its size is dictated by the effective volume through which most of the combustion products pass. Figure 3 illustrates the various heat fluxes entering and leaving a zone. The heat fluxes are identified as follows.

In-Fluxes

$\dot{Q}_{ch}$ = Chemical heat released by combustion of the fuel. Total chemical heat in the fuel may be released in more than one zone.

$\dot{Q}_{rec} + 1$ = Heat entering the zone because of recirculation of hot gases from the next zone

$\dot{q}_r$ = Radiative heat transfer from adjacent zones

$\dot{q}_{wr}$ = Radiative heat transfer from the hot gray furnace walls

$\dot{Q}_{sens}$ = Sensible heat entering the zone from preceding zone

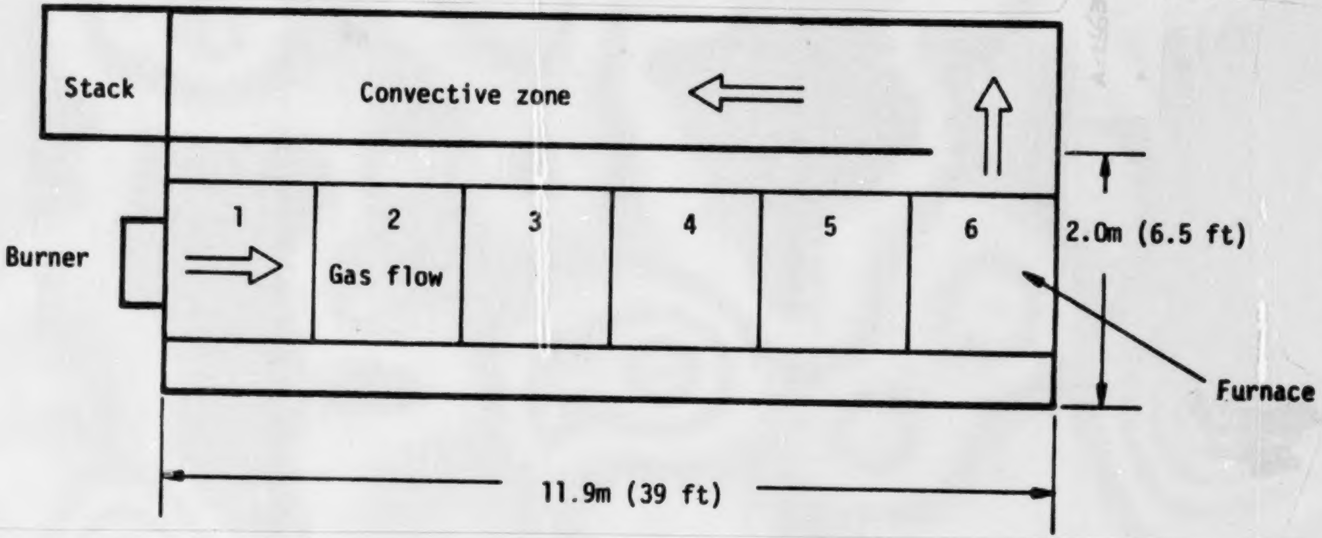
Stack
Convective zone
Burner
1
2
Gas flow
3
4
5
6
2.0m (6.5 ft)
Furnace
11.9m (39 ft)

Figure 2. Plan view schematic of package watertube boiler 44 MW (150 million Btu/hr) capacity; furnace height = 2.7m (9 ft).

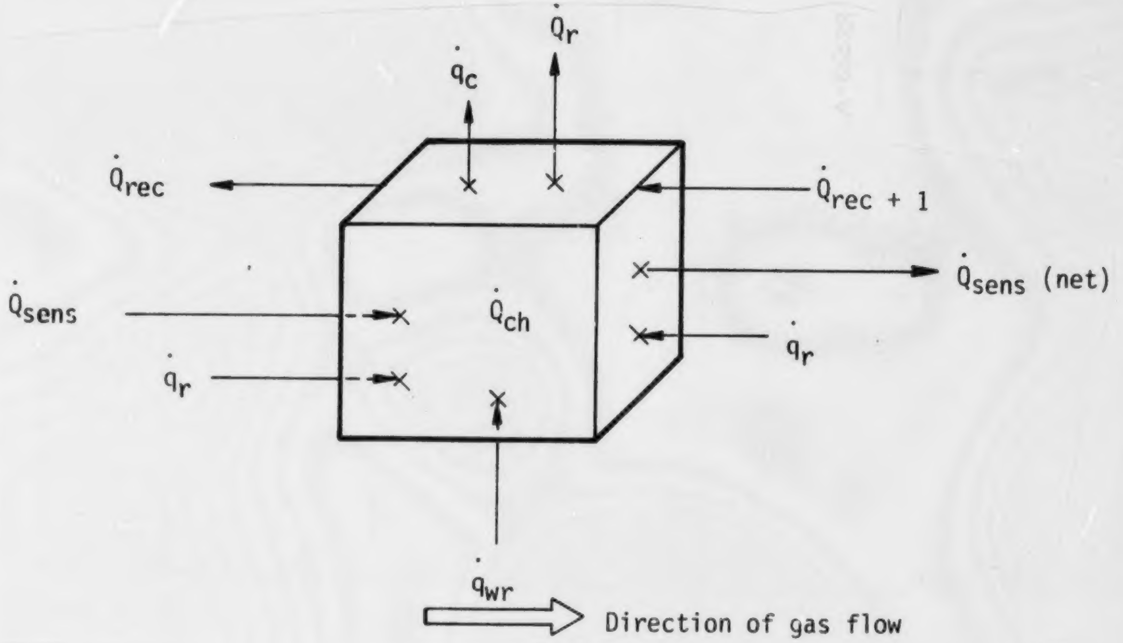
$\dot{Q}_r$
$\dot{q}_c$
$\dot{Q}_{rec}$
$\dot{Q}_{rec} + 1$
$\dot{Q}_{sens}$ (net)
$\dot{Q}_{sens}$
$\dot{Q}_{ch}$
$\dot{q}_r$
$\dot{q}_r$
$\dot{q}_{wr}$
Direction of gas flow

Figure 3. Schematic of a zone and heat fluxes.

Out-Fluxes

$\dot{Q}_r$ = Radiative heat transfer to the furnace walls enclosing the zone

$\dot{q}_c$ = Convective heat transfer to the furnace walls enclosing the zone

$\dot{Q}_{rec}$ = Heat leaving the zone because of recirculation of hot gases into preceding zone

$\dot{Q}_{sens}$ (net) = Net sensible heat leaving the zone and entering next

Thus, the energy balance equation takes the following form:

$$\dot{Q}_{sens}\ (net) = \dot{Q}_{sens} + \dot{Q}_{rec} + 1\ \dot{q}_r + \dot{q}_{wr} + \dot{Q}_{ch} - \dot{Q}_{rec} - \dot{Q}_r - \dot{q}_c \qquad (5\text{-}1)$$

This expression for net sensible heat allows for a solution for the bulk gas temperature leaving one zone and entering the next. Given an initial set of conditions, an iterative routine was used to solve for the gas temperature as a function of the axial distance along the furnace. The criteria for convergence was that the temperature change at any position on successive iterations was less than 14K (25°F). The calculated exit flue gas temperature was then compared with the boiler manufacturer suggested exit temperature. When these temperatures differed significantly (e.g., ±65K (±100°F)), the input assumptions were reevaluated.

Three sets of initial conditions have a major effect on the temperature profile of combustion gases in the furnace. These are the emissivity of the gas in each zone, the convective heat transfer in each zone, and the percent of gas recirculating from one zone into the preceding one. The gas cloud emissivity and its variation through the furnace is the most significant parameter for determining the temperature profile because of the significant role radiation plays in the transfer of heat to the furnace walls and, thus, the cooling rate of the gas.

Gas Cloud Emissivities

Calculations of flame emissivities for a mixture of gas and soot was developed as follows (Ref. 38):

$$\epsilon_m = \sum_n a_{gn}\ (T)(1 - \exp(-K_n L) \qquad (5\text{-}2)$$

Where a_{gn} is the fractional amount of energy in the n spectral regions where a gas of absorption coefficient K_n exists, and L is the path length representing the linear dimension that defines the cloud size. The absorption coefficient, K_n, is given for both gas and soot in each spectral region as:

$$K_n = k_{sn} C + k_{gn}(p_c + p_w) \tag{5-3}$$

where k's represent specific absorption coefficient with subscript s for soot and g for gas, and p_c and p_w are the partial pressures for CO_2 and H_2O, respectively. For gas clouds from combustion of natural gas $p_w/p_c \approx 2.0$, while for oil and coal combustion $p_w/p_c \approx 1.0$.[40] C is the concentration of soot particles in mass per unit volume.

A number of investigators have found considerable variation in the absorption coefficient depending on the type of flame, combustion history, flow, and mixing characteristics (Ref. 41). During this study, absorption coefficients used to develop gas cloud emissivities were estimated based on published data from experimental measurements and known combustion properties of different fuels. This greatly simplified the application of the model without significant impact on the temperature profile solutions. The zone emissivity was then calculated based on the relationship:

$$\varepsilon = 1 - \exp(-fkL) \tag{5-4}$$

where L is the path length defined in the zone method as the linear dimension used to define the cloud size, and f is the zone shape factor listed in Table 22 for each of the zone shapes used in this study. Resulting emissivities compared well with those published in a number of studies specific to both pilot-and full-scale industrial furnaces (Ref. 39, 42-44).

Convective Heat Transfer

Natural and forced convection heat transfer plays a less significant role than radiation in a boiler furnace. In the burner zone, where flame radiation is highest due to the presence of soot particles and high temperature radiating gases, convection accounts for less than 10 percent of the heat flux (Ref. 39). As the temperature is reduced and radiative properties of the gases decrease with burnout of soot and reduced temperature along the axial path of the furnace, convective heat transfer plays an increasing role. However, it still generally remains less significant than radiation.

Natural and forced convection between a fluid and an adjacent surface having a temperature gradient ΔT is expressed as:

TABLE 22. APPROXIMATE EMISSIVITY RELATIONS FOR A UNIFORM ISOTHERMAL CLOUD (REF 39)

Cloud or zone shape	Linear dimension used to define cloud size	Shape factor f		
		kL = 0	kL = 1	kL = 2
Convex cloud of arbitrary shape (used for stoker)	Ratio of volume to surface	4	3.4	3.4
Cube (used for all watertube units except the stoker)	Edge length	0.67	0.59	0.58
Cylinder (used for firetube boiler)	Diameter	0.67	0.64	0.61

$$\dot{q}_c = Nu\ k\ \Delta T/L \tag{5-5}$$

where Nu is the dimensionless Nusselt number given by the equations (Ref. 39):

$$Nu = 0.13\ (Gr)(Pr)^{1/2} \tag{5-6}$$

for watertube boilers and

$$Nu = 0.023\ (Re)^{0.8}\ (Pr)^{0.4}\ (1 + Re^{0.7}) \tag{5-7}$$

for firetube boilers, and k is the thermal conductivity of the gas. Gr, Pr, and Re are the Grashof, Prandtl, and Reynolds numbers, respectively, evaluated at the temperature near the combustor waterwall surface. These Nusselt numbers were used in the convective heat flux model.

Chemical Heat Release

The heat released by the combustion of the fuel occurs in more than one zone. Thus, it is relatively important to estimate how much of the fuel is burned in each zone. The heat of reaction can be represented by an exponential curve which has a value of zero at the burner throat and

99-percent completion by the end of the flame. Most of the heat is liberated near the burner to achieve a stable flame pattern.

As a guide, the mathematical model assumed a flame envelope of 0.2 m^3 (7 ft^3) for each MW of thermal heat input (Ref. 44). The length of the flame is a function of its diameter, which in turn varies according to the degree ofswirl imparted by the burner register settings. For the firetube units, the flame diameter was assumed to be 0.61m (2 ft). For the larger capacity watertube boilers, the flame diameter was assumed to be 1.37m (4.5 ft). These dimensions resulted in flame lengths of about 3.05m (10 ft) for the firetubes and about 5.9m (20 ft) for the package watertube boilers, corresponding to over half the furnace length. These results are in good agreement with visual observation of burner flames in industrial boiler furnaces.

Gas Recirculation

Recirculation of hot combustion gases is of particular importance because it serves to carry heat to the incoming reactants, thus raising the temperature to ignition levels. Recirculation in small industrial boiler furnaces such as firetube boilers can be as high as 50 percent of the total mass throughput (Ref. 38). The magnitude is a function of the furnace geometry and degree of swirl imparted to the combustion air.

In the mathematical model, no attempt was made to calculate the magnitude of the recirculating combustion products from one zone into the preceding one. The magnitude was crudely estimated based on published data for applications of the zone method for small industrial boilers (Ref. 38). For the boilers studied in this program, the magnitude of the recirculating gas never exceeded 30 percent and only affected the near burner region where turbulence is normally highest. This simplification in estimating the recirculation of the flue gas did not affect the usefulness of the solutions.

5.2.1.2 Bulk Residence Time Calculations

The time an elemental gas volume or particle in the flue gas remains in the furnace depends on the path it follows in passing through the furnace. The plug flow model modified by a degree of mixing is a good approximation to the gas flow in most boiler furnaces. In the plug flow model, the basic assumptions are that the combustion products flow through the furnace without any longitudinal mixing and that the temperature, composition, and velocity are uniform at any one cross section of the furnace.

The residence time distribution in a plug flow reactor modified by a degree of mixing is illustrated in Figure 4. Here, $F(t)$ is the fraction of gas residing in the furnace for less than the time t, and $\bar{t}$ is the bulk mean residence time (defined as the furnace volume divided by the volume flowrate). Experimental measurements indicate that some gas will exit the furnace by a time of $t = 0.5\bar{t}$. Virtually all the flue gas would have exited by a time $t = 2\bar{t}$ (Ref. 35). The minimum residence time of $0.5\bar{t}$ is important

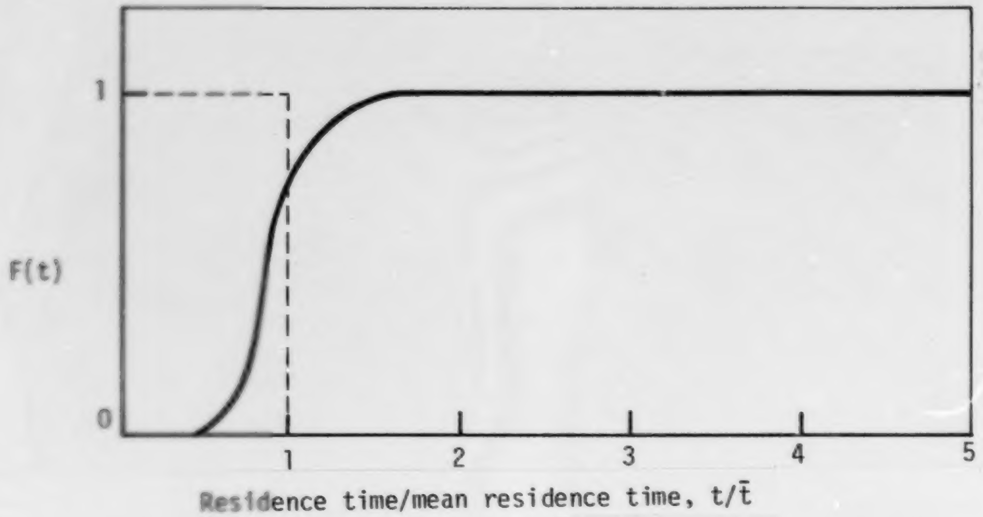

Figure 4. Residence time distribution in plug flow modified by a degree of mixing (Ref. 39)

in estimating the degree of combustion efficiency of the fuel as well as the degree of destruction of the hazardous wates considered in this study.

Residence times reported in the following sections are mean residence times ($\bar{t}$) calculated based on a total furnace volume from the burner region to the exit plane of the furnace. In reality, the total volume of the furnace is not utilized by the combustion products, which results in a portion of the gas exiting at a time much less than $\bar{t}$. Longitudinal mixing and the presence of recirculating zones are the primary cause for portions of the gas remaining for times much greater than or less than $\bar{t}$. In fact, a small fraction of the flue gas may reside in the furnace almost indefinitely due to stagnant recirculating zones or "dead space."

5.3 INDUSTRIAL BOILER TEMPERATURE-TIME PROFILES

This section presents the temperature-time profiles obtained using the isothermal zone method described previously. Appendices A and B, which illustrate the division of the furnaces into zones and the computer listings of calculated results, respectively, are provided as general support material. Figures 5 through 18 illustrate the temperature-time profiles and the heat fluxes in the furnaces of the seven boilers surveyed in this study. Both full and half boiler heat input operating conditions are presented. The excess air (EA) levels were increased for the half load cases to account for the generally higher air/fuel ratios used during reduced boiler load operation.

The trends of both temperature and heat absorption results are similar for all the boilers. The temperature of the combustion products showed a

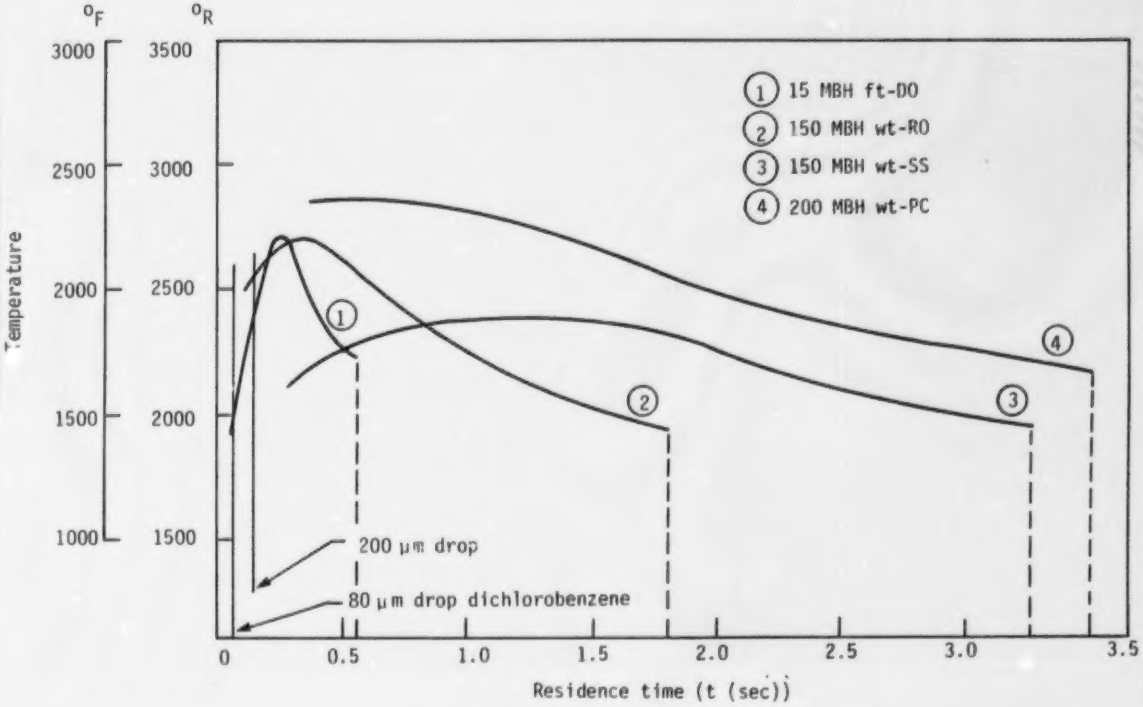

Figure 5. Temperature-time profile for the 58.6-MW (200 million Btu/hr) pulverized-coal-fired boiler (boiler G).

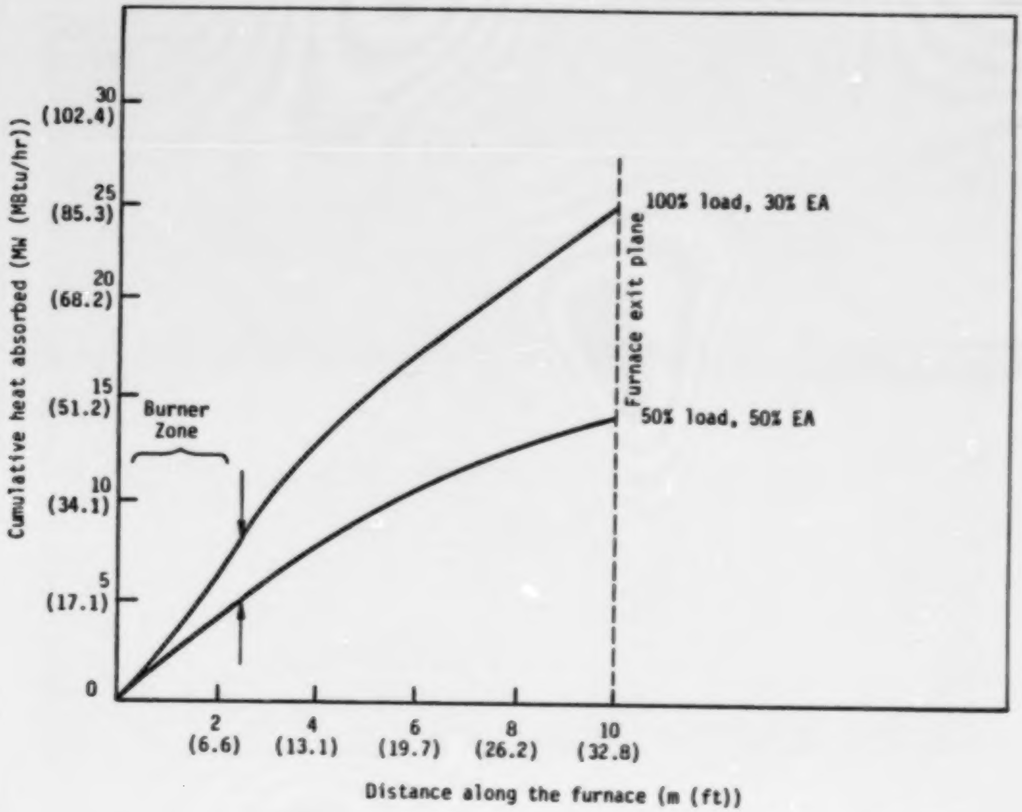

Figure 6. Cumulative heat absorption for the 58.6-MW (200 million Btu/hr) pulverized-coal-fired boiler (boiler G).

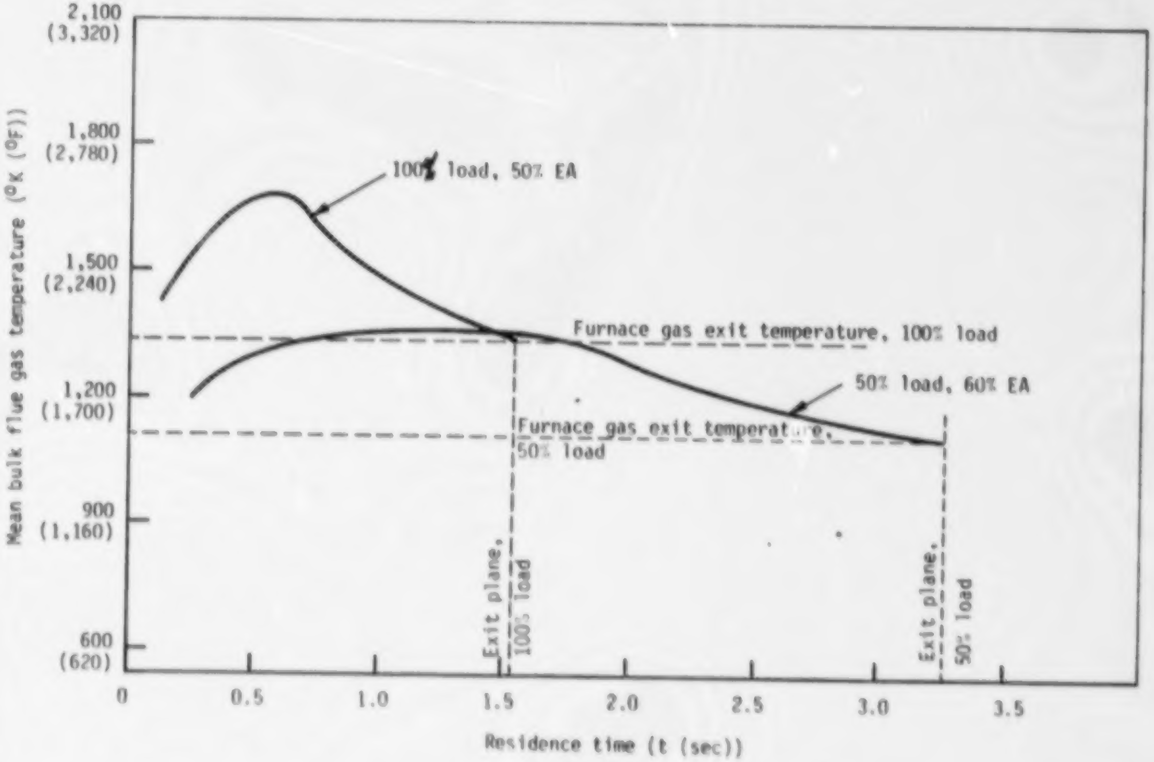

Figure 7. Temperature-time profile for the 44-MW (150 million Btu/hr) spreader stoker boiler (boiler F).

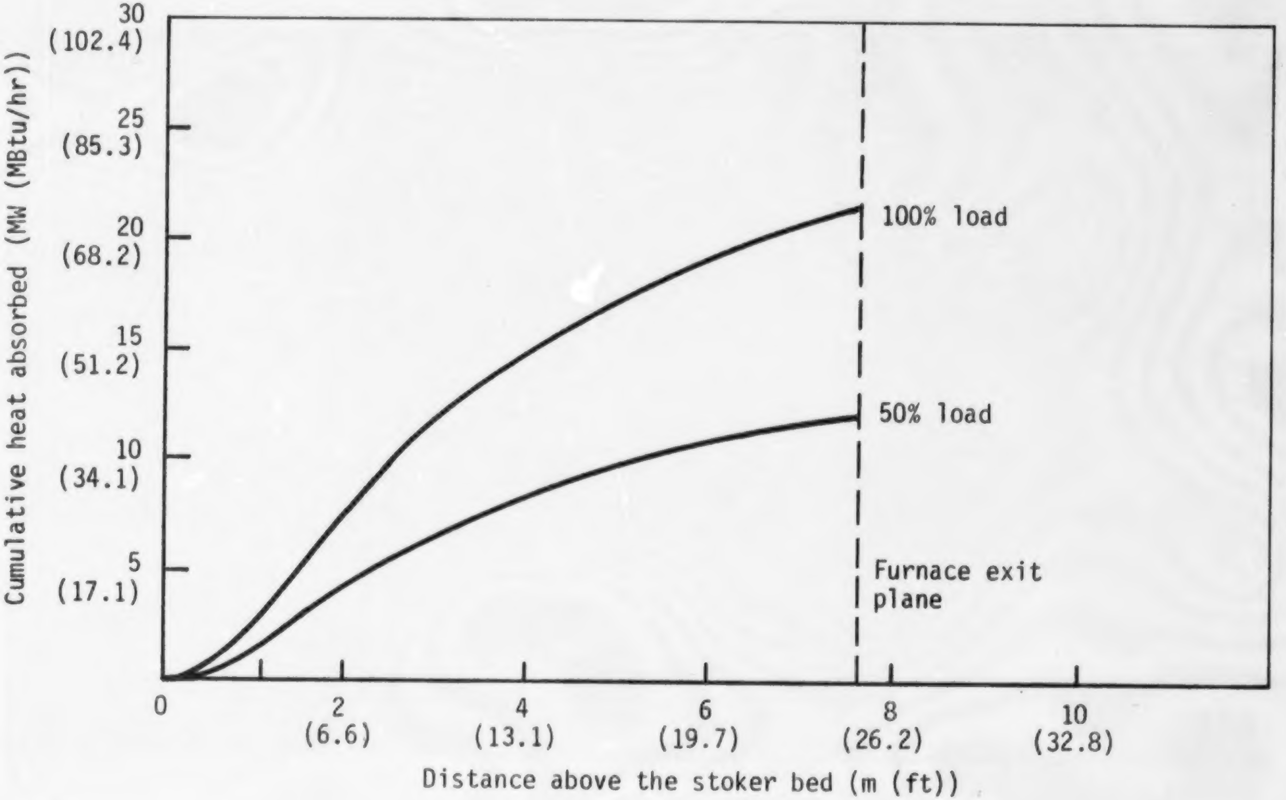

Figure 8. Cumulative heat absorption for the 44-MW (150 million Btu/hr) spreader-stoker boiler (boiler F).

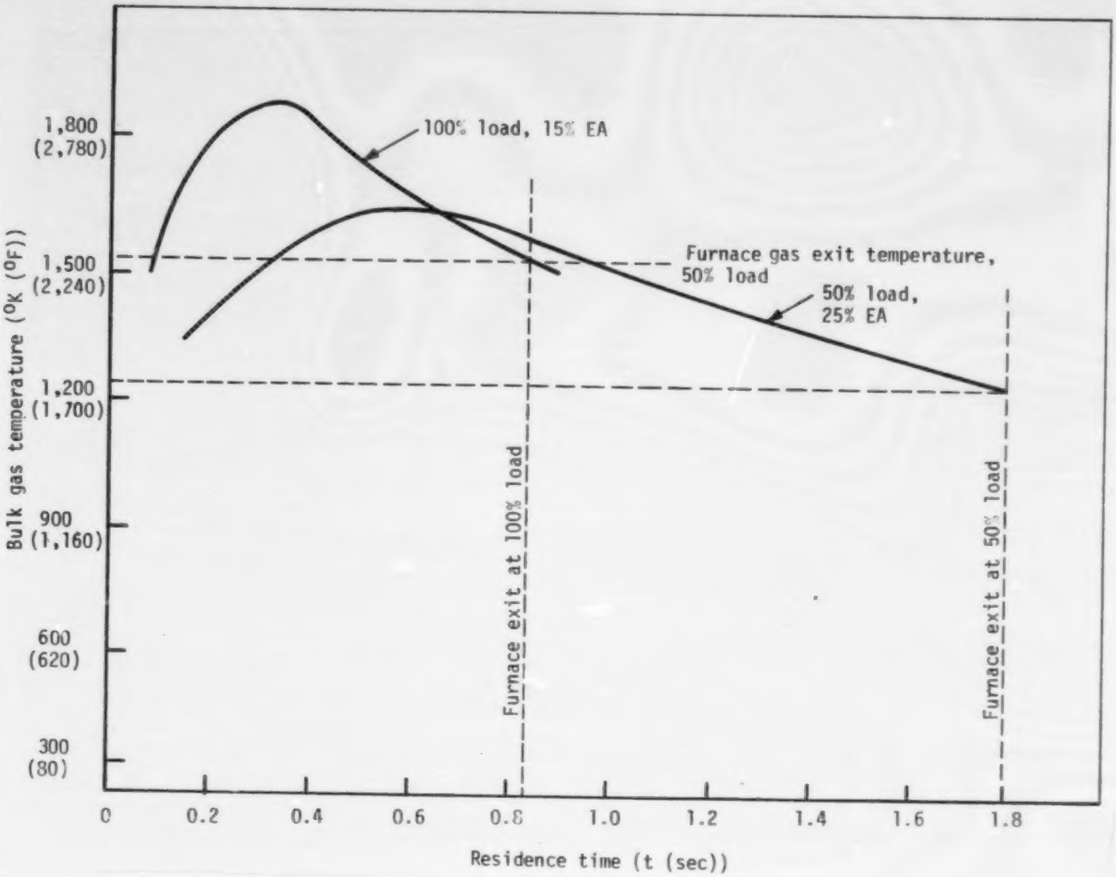

Figure 9. Temperature-time profile for the 44-MW (150 million Btu/hr) residual-oil-fired packaged boiler (boiler C).

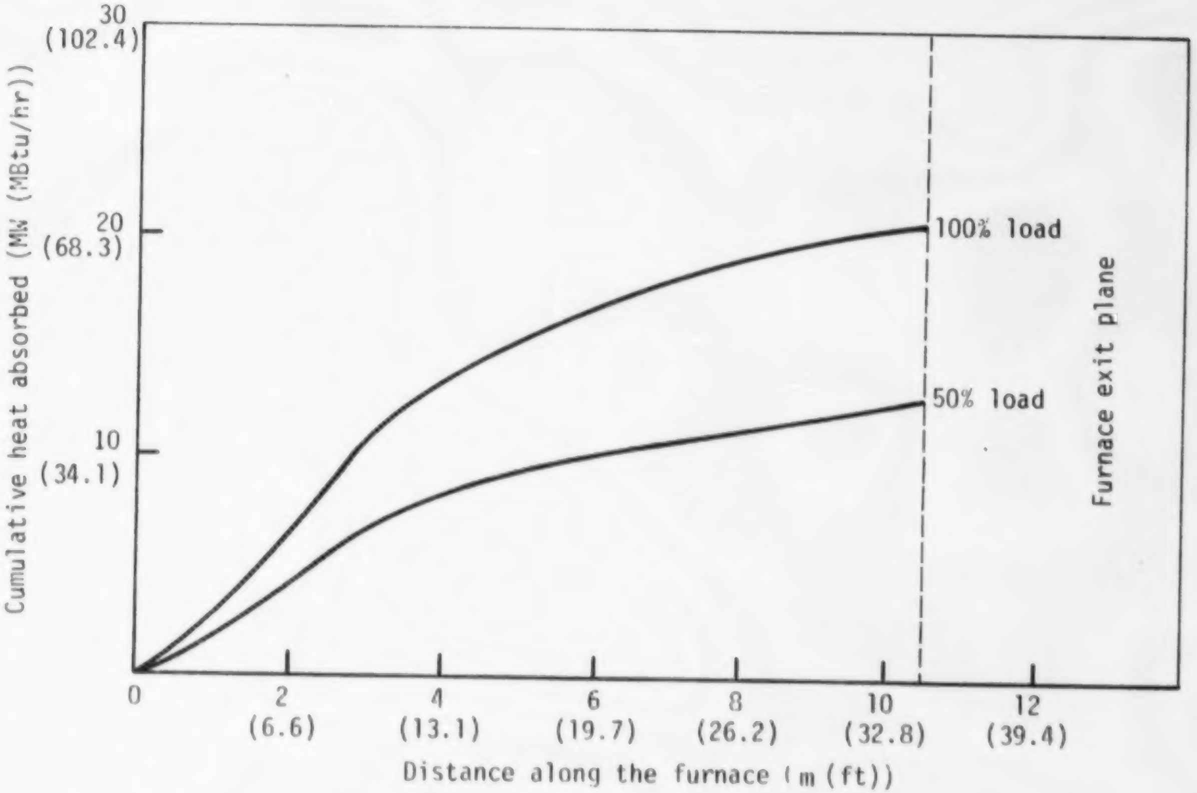

Figure 10. Cumulative heat absorption for the 44-MW (150 million Btu/hr) residual-oil-fired packaged boiler (boiler C).

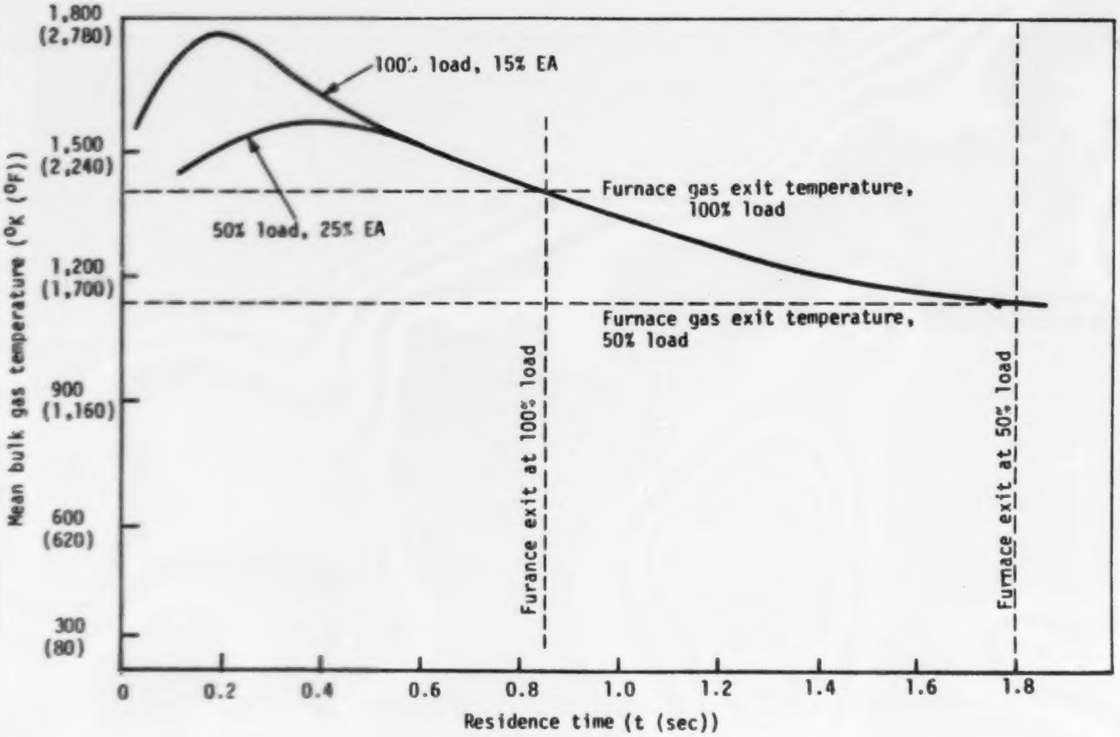

Figure 11. Temperature-time profile for the 44-MW (150 million Btu/hr) distillate-oil-fired packaged boiler (boiler D).

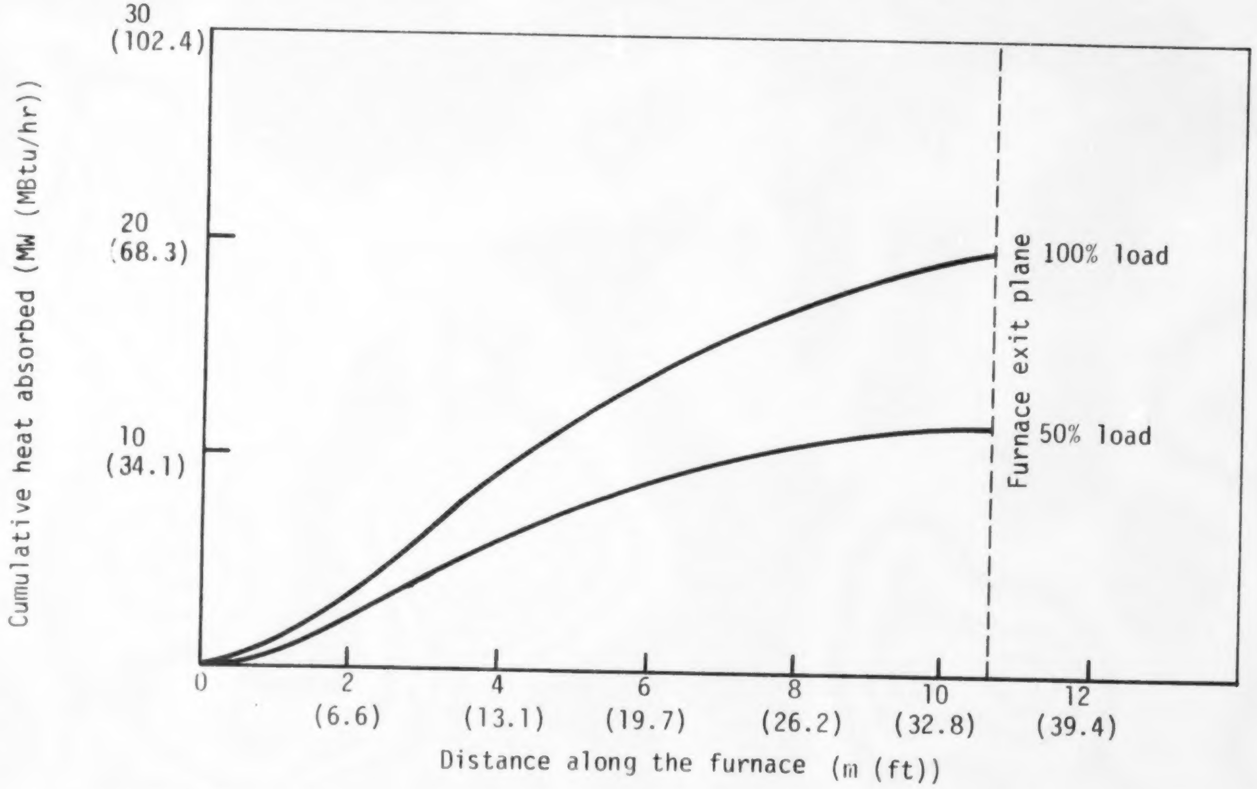

Figure 12. Cumulative heat absorption for the 44-MW (150 million Btu/Hr) distillate-oil-fired packaged boiler (boiler D).

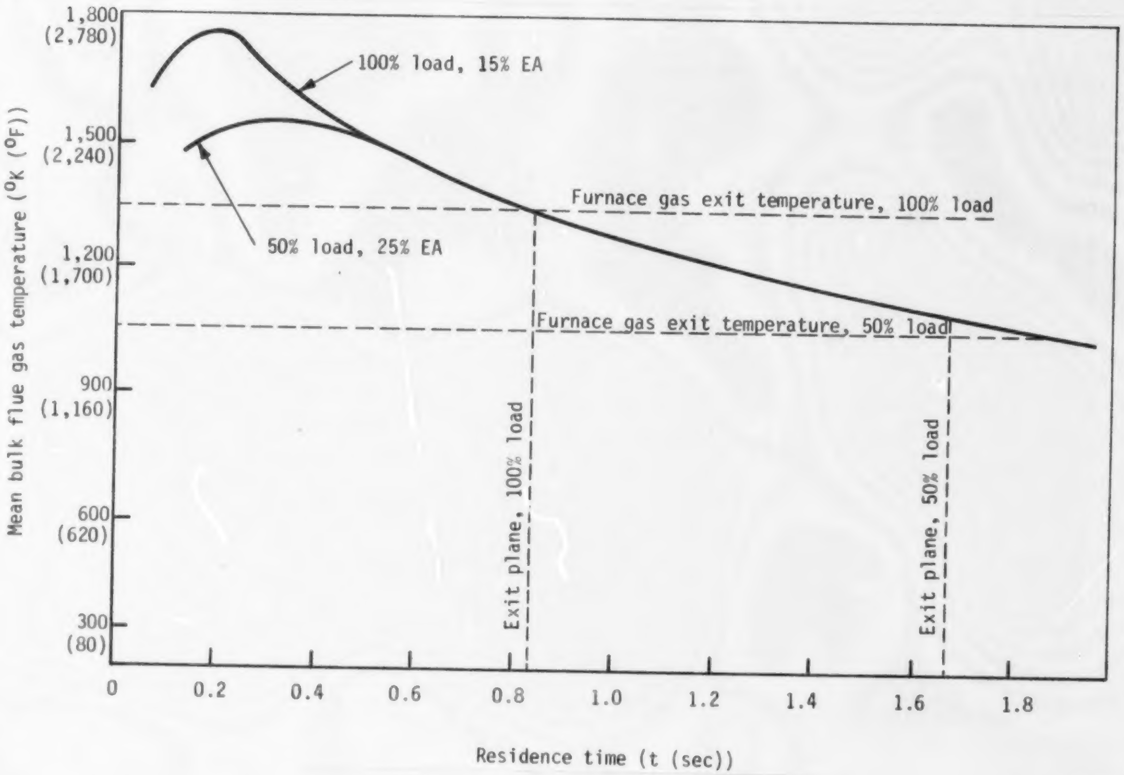

Figure 13. Temperature-time profile for the 44-MW (150 million Btu/hr) natural-gas-fired packaged boiler (boiler E).

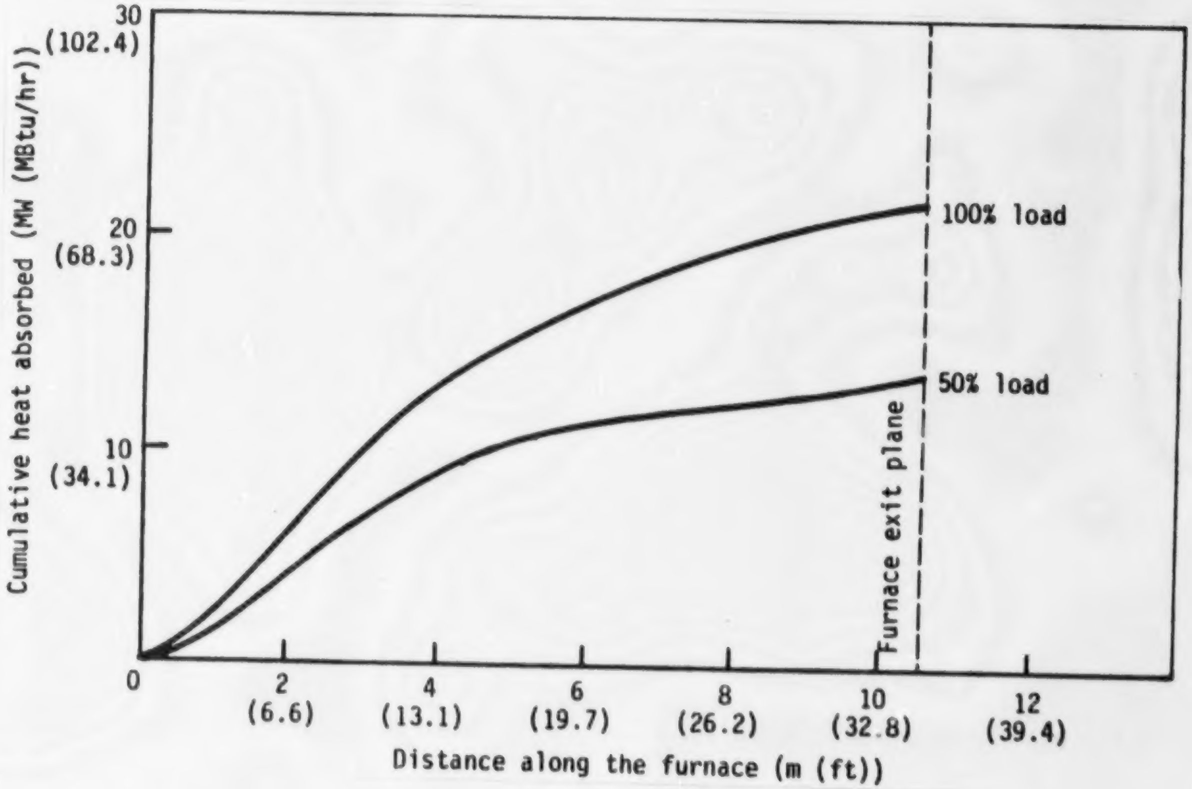

Figure 14. Cumulative heat absorption for the 44-MW (150 million Btu/hr) natural-gas-fired packaged boiler (boiler E).

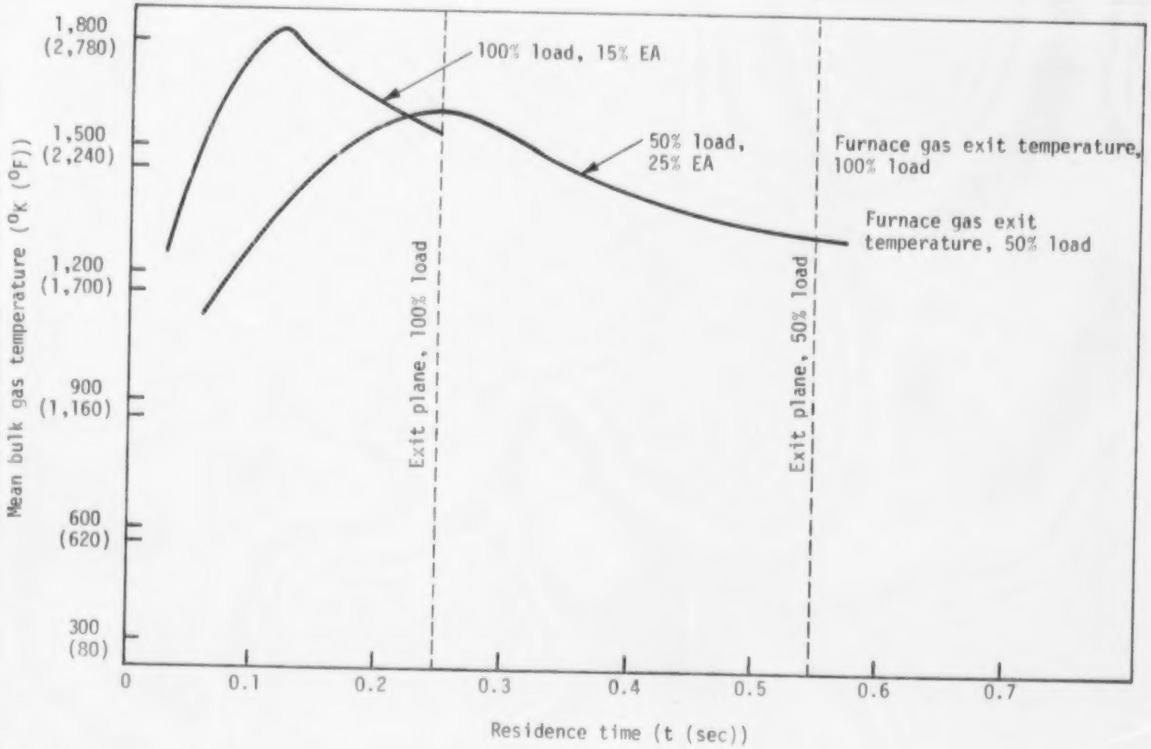

Figure 15. Temperature-time profile for the 4.4-MW (15 million Btu/hr) distillate-oil-fired firetube boiler (boiler A).

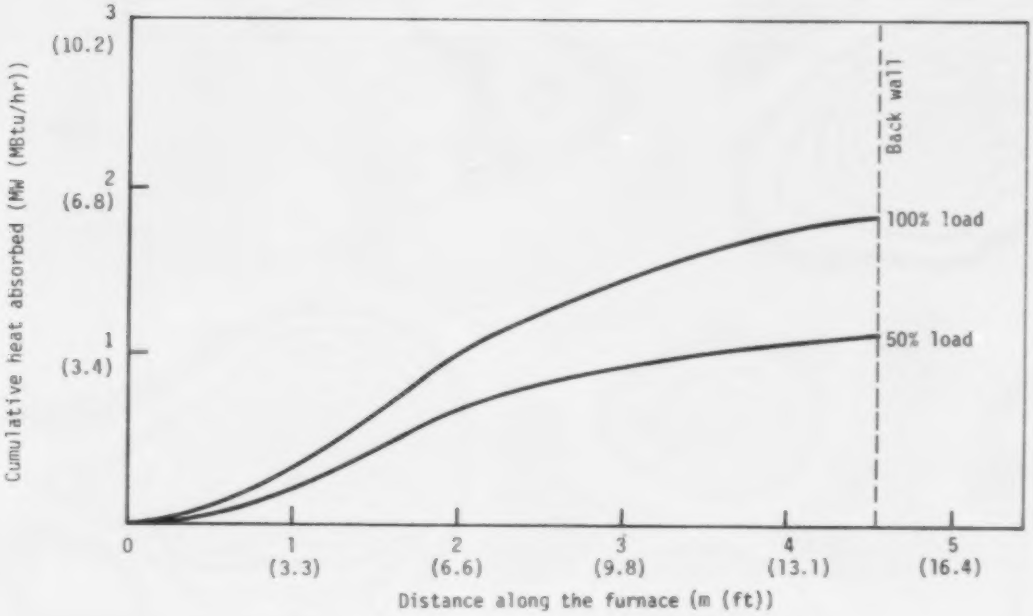

Figure 16. Cumulative heat absorption for the 4.4-MW (15 million Btu/hr) distillate-oil-fired firetube boiler (boiler A).

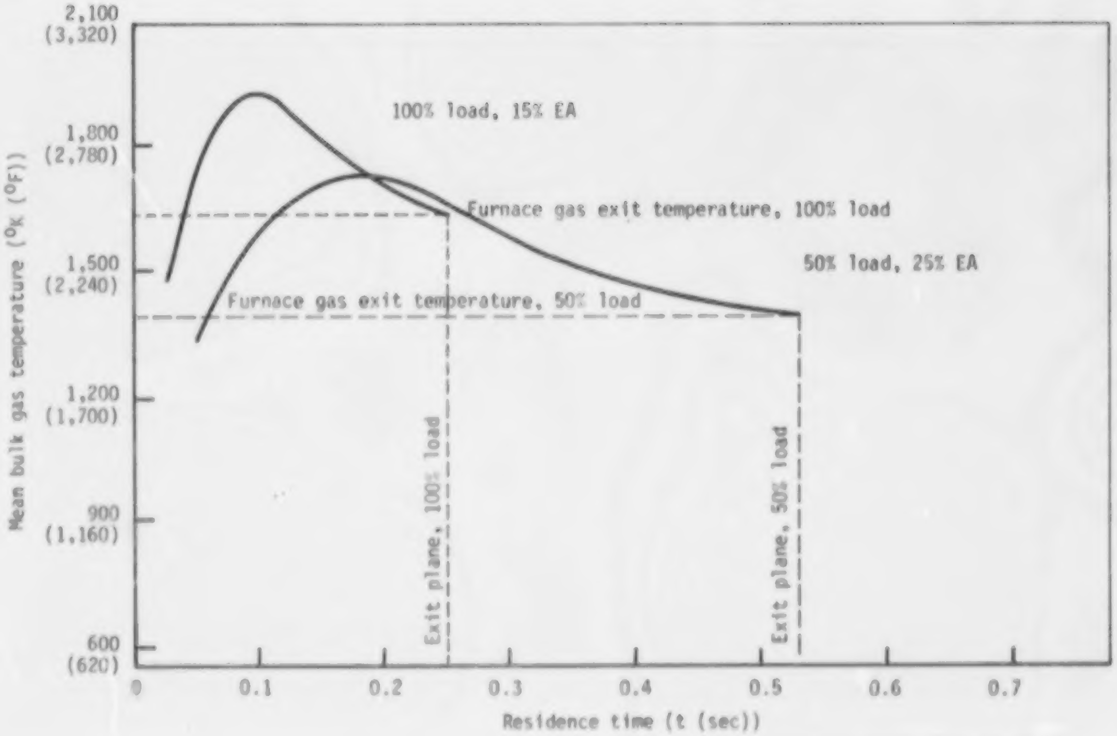

Figure 17. Temperature-time profile for the 4.4-MW (15 million Btu/hr) natural-gas-fired firetube boiler (boiler B).

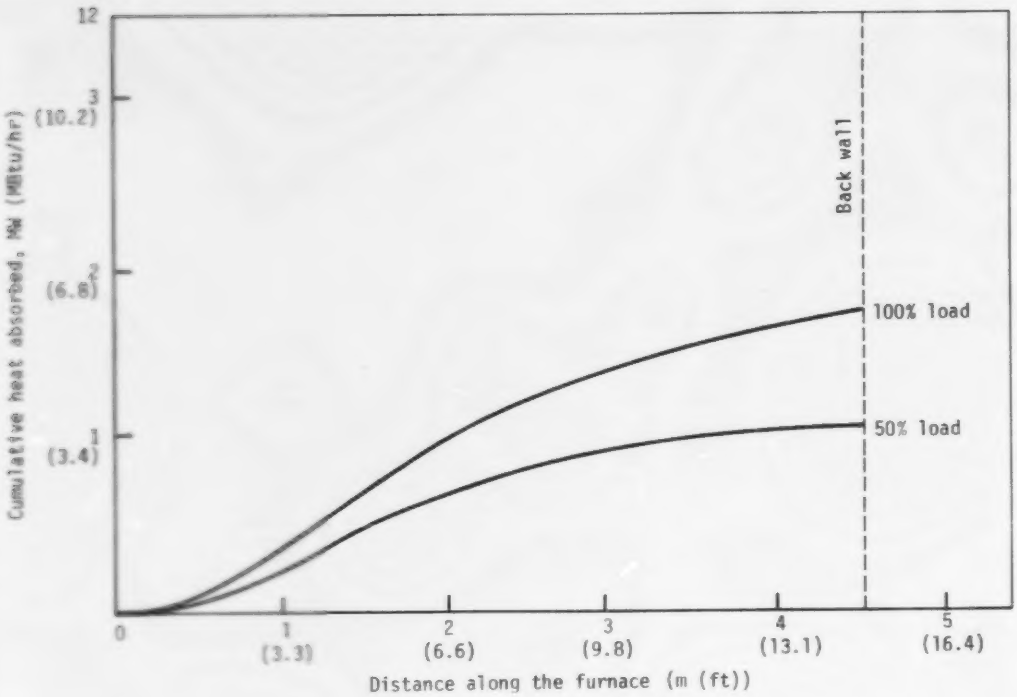

Figure 18. Cumulative heat absorption for the 4.4-MW (15 million Btu/hr) natural-gas-fired firetube boiler (boiler B).

peak in the near burner zone after which the temperature decreased nearly linearly to the furnace exit level. The heat flux to the furnace walls was highest in the burner zone where the heat release is high and turbulent mixing occurs. Downstream of this primary combustion region, the rate of heat absorption showed a decrease as the temperature and radiant heat transfer decreased. These results compare quite well with published data (Ref. 39,43,44)

The location of the temperature peak is primarily a function of the amount of heat released and the extent of combustion gas recirculation. In the case of the pulverized-coal-fired boiler (boiler G), the first computational zone encompassed the entire burner region (see Figure A-1, Appendix A). About 90 percent of the heat release was assumed to take place in the burner region. Gas recirculation from the second zone into the first was considered minimal since most of the turbulent mixing takes place within the burner region. Consequently, the gas temperature and the rate of heat absorption peaks in the first zone as illustrated in Figures 5 and 6.

For the spreader stoker unit (boiler F), Figures 7 and 8, the total heat release was distributed over the first three computational zones. Over 50 percent of the heat was assumed to be liberated in the first zone, close to the coal bed, while the remainder of the heat release was assumed to take place within the throwing region of the spreader.

Gas recirculation from the second to the first zone caused by the overfire combustion air jets, occurred at and above the stoker grate. The peak temperatures occurred at approximately 2.7m (8.8 ft) above the fuel bed which had a temperature of about 1,300K (2,030°F). Reducing boiler load to half of the heat input capacity resulted in the peak temperature occurring at approximately 3.8m (12.4 ft) above the stoker grate.

For both the package watertube and firetube units (boilers A through E), (Figures 9 to 18), the heat release was distributed over the calculated length of the flames. Gas recirculation and turbulent mixing were generally assumed to take place over half of the furnace length. Both the temperature-time profiles and heat flux distributions for these units are very similar, with the peak temperature occurring at a distance of about 2.7 to 4.6m (9 to 15 ft) and 2.3m (7.5 ft) downstream of the burner for the watertube and firetube units, respectively.

Tables 23 and 24 summarize the results of the heat transfer calculations outlining both peak and exit gas temperatures, bulk residence times, and heat transfer data for the full load and half load cases. A minimum residence time (0.5 times the mean time) is also listed based on arguments presented in Section 5.2. The highest temperatures occur as expected in the distillate-oil-and natural-gas-fired boilers because of the lower radiative properties of the combustion products from these fuels. Shortest residence times occur in the firetube boilers, which show the lowest percent of heat absorbed in the furnace.

TABLE 23. SUMMARY OF BOILER TEMPERATURE-TIME PROFILE DATA -- 100-PERCENT LOAD

	Gas temperature (°K (°F))		Residence time at furnace exit (sec)		Heat flux (MW (million Btu/hr))	
Boiler	Peak	Furnace exit	Mean, $\bar{t}$	Minimum $0.5\bar{t}$	Total heat absorbed in furnace	Percent of input
A: 4.4 MW (15 million Btu/hr) Natural-gas-fired firetube	1,815 (2,810)	1,600 (2,425)	0.25	0.13	1.56 (5.3)	36
B: 4.4 MW (15 million Btu/hr) Distillate-oil-fired firetube	1,710 (2,615)	1,490 (2,215)	0.25	0.13	1.62 (5.5)	37
C: 44 MW (150 million Btu/hr) Natural-gas-fired packaged watertube	1,815 (2,810)	1,475 (2,200)	0.83	0.42	19.3 (65.7)	44
D: 44 MW (150 million Btu/hr) Distillate-oil-fired packaged watertube	1,715 (2,630)	1,340 (1,955)	0.84	0.42	21.1 (72.0)	48
E: 44 MW (150 million Btu/hr) Residual-oil-fired packaged watertube	1,700 (2,600)	1,295 (1,875)	0.83	0.42	21.4 (73.1)	49
F: 44 MW (150 million Btu/hr) Spreader-stoker watertube	1,620 (2,450)	1,325 (1,925)	1.57	0.79	20.2 (69.0)	46
G: 58.6 MW (200 million Btu/hr) Pulverized-coal-fired watertube	1,790 (2,770)	1,435 (2,120)	1.75	0.88	22.3 (76.0)	38

TABLE 24. SUMMARY OF BOILER TEMPERATURE-TIME PROFILE DATA -- 50-PERCENT LOAD

	Gas temperature (°K (°F))		Residence time at furnace exit (sec)		Heat flux (MW (million Btu/hr))	
Boiler	Peak	Furnace exit	Mean, $\bar{t}$	Minimum $0.5\bar{t}$	Total heat absorbed in furnace	Percent of input
A: 4.4 MW (15 million Btu/hr) Natural-gas-fired firetube	1,630 (2,475)	1,335 (1,940)	0.53	0.27	1.0 (3.43)	46
B: 4.4 MW (15 million Btu/hr) Distillate-oil-fired firetube	1,515 (2,270)	1,235 (1,764)	0.55	0.28	1.03 (3.51)	47
C: 44 MW (150 million Btu/hr) Natural-gas-fired packaged watertube	1,575 (2,370)	1,210 (1,715)	1.78	0.89	11.7 (39.8)	53
D: 44 MW (150 million Btu/hr) Distillate-oil-fired packaged watertube	1,505 (2,250)	1,085 (1,495)	1.81	0.91	12.6 (43.0)	57
E: 44 MW (150 million Btu/hr) Residual-oil-fired packaged watertube	1,490 (2,220)	1,045 (1,425)	1.85	0.93	13.0 (44.5)	59
F: 44 MW (150 million Btu/hr) Spreader-stoker watertube	1,315 (1,910)	1,080 (1,490)	3.2	1.6	11.3 (38.6)	51
G: 58.6 MW (200 million Btu/hr)Pulverized-coal-fired watertube	1,585 (2,390)	1,195 (1,690)	3.5	1.8	12.9 (44.0)	44

5.4 EVALUATION OF CALCULATED TEMPERATURE-TIME PROFILES

The temperature-time profile solutions presented in this study should be used with care. The generic approach and assumptions used have resulted in the development of a model that, when properly applied, will lead to the generation of information. In evaluating the destruction efficiency of hazardous wastes in typical industrial boiler furnaces such as the ones considered in this study, it should be emphasized that a conservative use of these data be adopted. This conservative use consists essentially of taking the lowest temperature profile, such as the temperature gas profile close to the furnace waterwalls, and the least gas residence time. This combination, although inconsistent (i.e., the lowest temperature gas next to the furnace wall will have the longest residence time), represents conservatism. These conservative values can then be compared to the temperature and residence times required for thermal destruction of hazardous wastes as will be presented in Sections 6 and 7. If these data predict that a certain hazardous waste is destroyed in a given boiler type, a more extensive evaluation should be undertaken. This should include an assessment of of the boiler compatibility with the waste, secondary and fugitive emissions projections retrofit considerations, and a detailed economic analysis of the benefit of disposing of hazardous waste in industrial boilers over other disposal technologies. An overview of these considerations is presented in Section 8.

SECTION 6

THEORETICAL APPROACH TO THERMAL DESTRUCTION OF HAZARDOUS WASTES

The purpose of this section is to develop a mathematical expression predicting the time for the 99.99-percent destruction of a given hazardous waste as a function of a given boiler time and temperature profile. The approach will be to:

- Establish a physical/chemical model of the processes through which the hazardous waste must pass
- Generate a mathematical expression for each process
- Predict conservative time functions for each process
- Sum the time functions to establish the required residence time at boiler conditions
- Compare predicted residence times against experimental values

The word "conservative" implies that all assumptions should tend to maximize the time required for a particular process. Thus, the predicted total time for the conservative model should always exceed any experimentally determined times. This will ensure that if the model shows a particular boiler to be applicable, it can be assumed to achieve the required destruction.

6.1 THE QUALITATIVE MODEL

The model used consists of a series of steps. The steps are:

- Heating the hazardous waste to its boiling temperature
- Vaporizing the waste
- Heating the hazardous waste vapor to the boiler ambient temperature
- Destroying the waste constituents by one of two processes
    - -- Thermal cracking of the strongest bond
    - -- First-stage oxidation

Five simplistic destruction models incorporating these processes are represented schematically in Figure 19. The conservative nature of this qualitative picture is readily apparent. In each of the first four cases, it is assumed that:

- The material is brought to its boiling point before any other process takes place (i.e., volatilization from the surface)
- The material is completely vaporized before any succeeding process starts

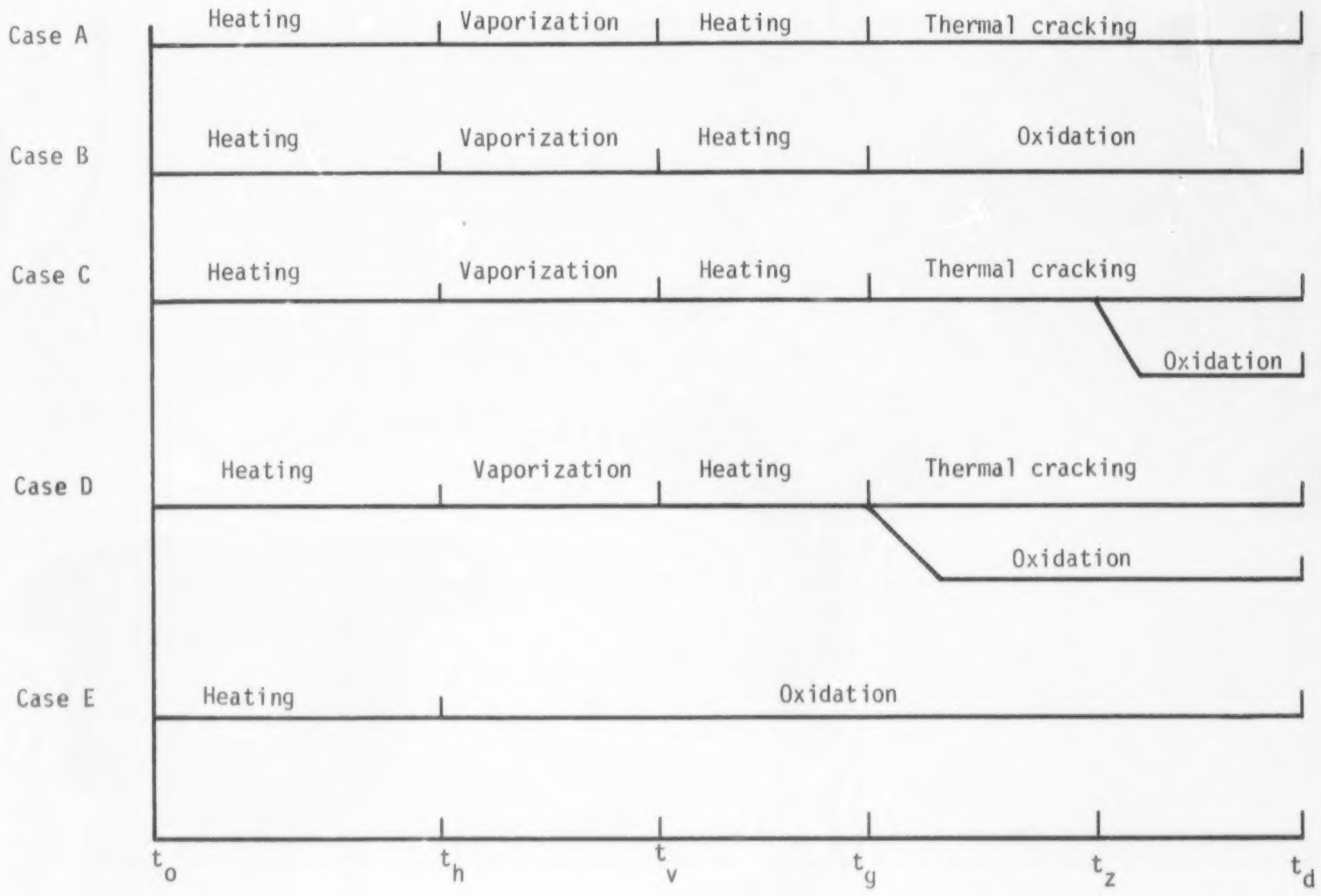
Case A
Heating
Vaporization
Heating
Thermal cracking
Case B
Heating
Vaporization
Heating
Oxidation
Case C
Heating
Vaporization
Heating
Thermal cracking
Oxidation
Case D
Heating
Vaporization
Heating
Thermal cracking
Oxidation
Case E
Heating
Oxidation
t_o
t_h
t_v
t_g
t_z
t_d

Figure 19. Processes for thermal destruction.

- All gas phase materials are heated to boiler ambient temperature before any destruction takes place

It is known that material ignites and burns (i.e., oxidizes) on its surface before complete volatilization occurs, and that diffusion limited burning of an expanding sphere of gas is also a normal boiler process. This process is depicted in case E of Figure 19 and is the least conservative.

6.2 THE QUANTITATIVE MODEL

A most conservative semiquantitative model for the destruction of hazardous waste materials can be easily formulated providing certain critical data are available. Without these data, conservative assumptions can be made that will also allow conservative prediction of degree of hazardous waste destruction.

The physical parameters determining destruction efficiency are time, temperature, and turbulence. The values of these parameters required to meet a certain efficiency are dependent on the destruction process (thermal cracking or oxidation) and the kinetic constants of the individual compound. If the time, temperature, and turbulence (which is related to oxygen availability) requirements to meet the required destruction efficiency of a given compound can be expressed mathematically, and if these can be compared to the time, temperature, and turbulence profile of a given boiler, then the ability of the boiler to achieve the desired destruction efficiency can be predicted.

The construction of the semiquantitative predictive model consists of:

- A series of assumptions
- A qualitative model chosen from those laid out in the previous section
- A theoretical mathematical expression generated that predicts the time and temperature requirements for 99.99-percent destruction
- A boiler time and temperature expression generated that can be compared to compound's time and temperature requirements

6.2.1 Choice of Model

The destructive processes of significance in thermal destruction are thermolytic cracking (pyrolysis) and oxidation. Another process, certain to occur in a boiler environment, is flame oxidation. Flame process rates are much faster than either thermal pyrolysis or oxidation reactions. However, so little rate data exist for these processes, that they are not considered herein.

Without reference to products of incomplete combustion, the parameter of concern is the disappearance of a particular hazardous waste component. The first step of destruction by pyrolysis is the homolytic thermolysis of a bond. In oxidation, it is either the radical abstraction of a hydrogen atom by oxygen, or the insertion of an oxygen radical into the molecule.

Pyrolysis is first-order kinetics (Ref. 45), while first-stage oxidation can be approximated by pseudo-first-order kinetics. (Ref. 46) Pyrolysis is the slower of the two processes. Thus, case A of the qualitative models is chosen as the most conservative approach.

6.2.2 Mathematical Formulation for Rate of Destruction

Assuming that the hazardous waste is in the gas phase, the rate of disappearance of a hazardous waste constituent by pyrolysis can be expressed as:

$$\frac{dC_A}{dt} = -kC_A \qquad (6\text{-}1)$$

where C_A is the concentration of the material at time t and k is the temperature dependent rate constant. Solution of this equation leads to:

$$\ln \frac{C_A}{C_{A_o}} = -k\Delta t \qquad (6\text{-}2)$$

where C_{A_o} is the initial concentration of material.

The rate constant k is given by the Arrhenius rate expression.

$$k = A \exp(-E/RT) \qquad (6\text{-}3)$$

where

A = Arrhenius pre-exponential frequency factor (sec^{-1})
E = Energy of activation for bond rupture (cal/mole)
R = Gas constant (1.987 cal/mole-K)
T = Temperature (K)

For 99.99-percent destruction, the concentration term is:

$$\ln \frac{C_A}{C_{A_o}} = -9.21 \qquad (6\text{-}4)$$

Substitution into Equation (6-2) and solving for Δt gives:

$$\ln \Delta t = \ln \frac{9.21}{A} + \frac{E}{RT} \qquad (6\text{-}5)$$

which is just the time and temperature expression necessary for 99.99-percent destruction.

6.2.3 Boiler Time-Temperature Relationship to Destruction Efficiency

A typical boiler time and temperature profile is shown in Figure 20. If isotherms (lines of equal temperature) are drawn across the profile, and their intersection dropped to the time coordinate, increments of time for which the gas is above a given temperature can be determined, as shown in Figure 21.

If these time increments are plotted against their corresponding isotherms, a curve relating time at or above a given temperature for the boiler can be obtained. During the temperature rise portion in the boiler, the time-temperature relationship is approximated by:

$$T = a + b \ln t_1 \qquad (6\text{-}6)$$

while during the fall it is:

$$T = c \exp Dt_2 \qquad (6\text{-}7)$$

The incremental time above a given temperature, $\Delta t_T m$ is $t_2 - t_1$. Algebraic manipulation gives:

$$\Delta t_T = \frac{1}{D} \ln \frac{T}{c} - \exp \frac{T-a}{b} \qquad (6\text{-}8)$$

Plotting T versus ΔtT gives the solid curve in Figure 22. Using Equation (6-5) and plotting T versus Δt for a given compound gives the dashed lines in Figure 22.

If any point on the compound line falls below the boiler curve, the boiler has sufficient time at high enough temperature to achieve 99.99-percent destruction.

In Figure 22 three hypothetical compound time-temperature requirements have been plotted. Compound A demonstrates a case where 99.99-percent destruction most probably will not be achieved. Compound B shows a case where destruction will be achieved if the material follows the mean time-temperature profile of the boiler. Compound C presents an example where destruction will always be achieved.

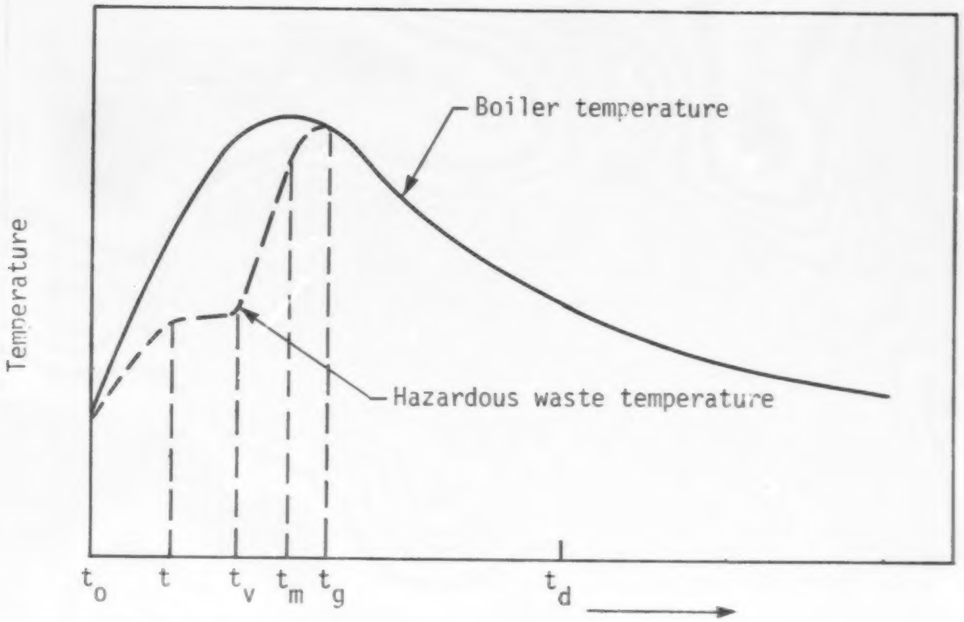
Boiler temperature
Hazardous waste temperature
Temperature
t_o
t
t_v
t_m
t_g
t_d

Figure 20. Waste material time-temperature path superimposed on boiler temperature profile.

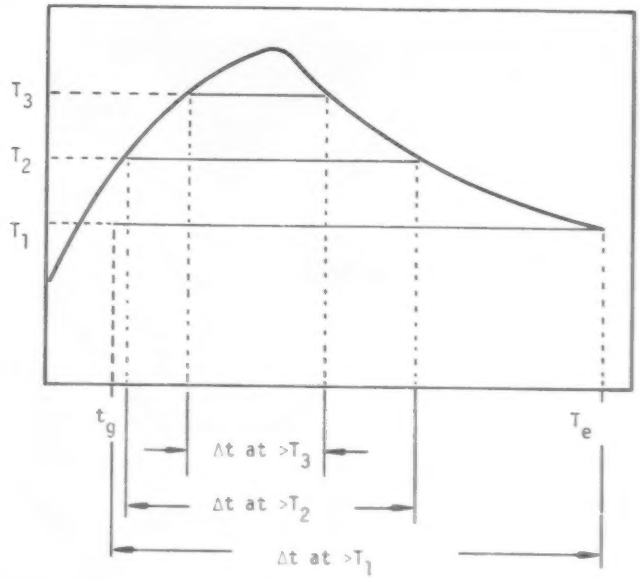
T_3
T_2
T_1
t_g
T_e
Δt at $>T_3$
Δt at $>T_2$
Δt at $>T_1$

Figure 21. Determination of time-above-temperature points.

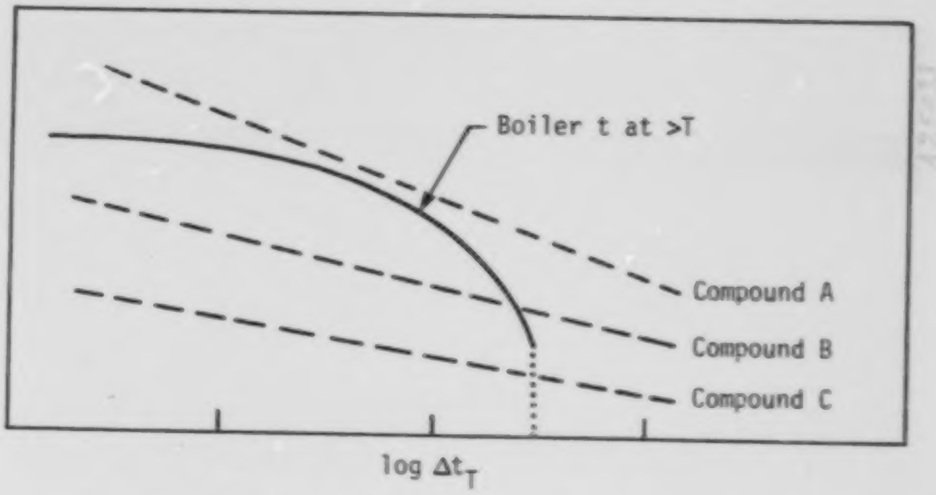

Figure 22. Hypothetical boiler time-above-temperature curve (solid curve) and compound destruction time-temperature curves (dashed curve).

6.3 MAKING PREDICTIONS

The following two subsections give two conservative approaches to destructibility predictions using the above model. The first is the most conservative case, and immediately classifies the compounds (or wastes) into a yes-no-maybe category. The second, extended conservative case refines the maybe category. Both cases assume the material is in the gas phase by the time of maximum temperature under the given boiler conditions. The determination of the validity of this assumption is discussed in Section 7.4.

One can assume that all volatile material is vaporized by the time (t_m) the maximum mean temperature in the boiler (T_m) is reached, since the maximum rate of heat release (combustion) has occurred. Also, as discussed in Section 5.2 the shortest residence time in a boiler is approximately one-half the mean residence time (t_e)(Ref. 39), and the lowest temperature path has a temperature maximum (T'_m) about 100K below T_m (Ref. 39).

6.3.1 Most Conservative Case

If a component is in the gas phase at time t_m in the boiler, and if the fastest path through the boiler is one-half the mean residence time, it is axiomatic that the component will be at or above the exit temperature for at least the time ($0.5\ t_e - t_m$). Given, then, the following information:

- Boiler mean residence time
- Boiler exit temperature
- Boiler mean time to maximum temperature
- Component kinetic A and E values

the material can be 99.99 percent destroyed if:

$$\ln (0.5\ t_e - t_m) > \ln \frac{9.21}{A} + \frac{E}{RT_e} \qquad (6\text{-}9)$$

A solution to the relationship between boiler time-above temperature and 99.99 percent destruction can be found that predicts components for which 99.99 percent destruction will certainly be achieved. This is accomplished by recognizing that for some particular set of E and A values the will be tangent to (or equal to the derivatives of) the boiler component curve time-above-temperature curve. The solution is:

$$\left[\left(\frac{E}{2R}\right)\left(-1 + \sqrt{1 + \frac{4RT_m}{E}}\right) - T_m\right]\left(\frac{t_e - t_m}{T_e - T_m}\right) > \frac{9.21}{A}\ \exp\left[2\left(-1 + \sqrt{1 + \frac{4RT_m}{E}}\right)^{-1}\right] \qquad (6\text{-}10)$$

Thus, for any set of component and boiler parameters meeting this relationship, the material will meet 99.99 percent destruction. All other cases are of the "maybe" category. Their relationships are further developed in Section 7.5, and demonstrated graphically for various hazardous waste stream and boiler parameters.

6.3.2 Extended Conservative Approach

In reality, the material will always be at temperatures above the exit in temperature. Because the rate of destruction is exponentially related to temperature, this should be taken into account when estimating destruction and removal efficiencies. One approach is to plot the curve of Equation (6-8) and the thermodynamic destruction curve and compare. However, with the assumption all waste constituents are in the gas phase at t_m, the equation can be simplified to use readily available parameters.

The temperature decay after T_m is approximately linear with time to the exit temperature (T_e). Thus, the increment of time, Δt, that a component will be above temperature, T, is given by:

$$\Delta t = (T - T_m)\frac{t_e - t_m}{T_e - T_m} \qquad (6\text{-}11)$$

The absolute minimum time increment, Δt, that a given material is above a given temperature, T, in the boiler is thus found by substituting 0.5 t_e for t_e, and $T_m' = T_m - 100K$ for T_m, with the temperature bounds $T_m' > T \geq T_e$. This is the "fast path" temperature profile.

Since the increment of time required for 99.99-percent destruction is given by Equation (6-5), if:

$$\ln \Delta t > \ln \frac{9.21}{A} + \frac{E}{RT} \qquad (6\text{-}12)$$

(where Δt is calculated by Equation (6-11) for fast path values), the boiler will achieve 99.99-percent destruction. It is easiest to simply plot Equations (6-11) and (6-5) to see if Equation (6-5) falls below Equation (6-11) at any point. A plot similar to Figure 22 will be obtained.

The extended conservative estimate of a boiler's capacity to destroy a given hazardous waste is achieved in the following manner:

- For given boiler conditions, the time increment is plotted against the temperature (Equation (6-11)
- For a given hazardous waste compound, the curve of Equation (6-5) is plotted on the same graph
- If any point of the boiler curve falls above the compound curve, the boiler will give 99.99-percent destruction of the compound

6.4 STREAM SELECTION

Stream selection for evaluation with respect to boiler destructibility was based on three principal criteria:

- Those streams intuitively thought to be able to be destroyed (i.e., those streams that were primarily organic in nature)
- Streams that were reasonably well characterized (with respect to composition and physical properties) in the available literature
- Streams covering a wide variety of classes of organic compounds

Table 25 lists the streams identified for evaluation and the classes of compounds contained. Table 26 gives composition information on each stream. (Note: Stream K012, acrylonitrile still bottoms, is no longer classified as a hazardous waste stream. It is used here because of the compound class.)

In actuality, there are several perturbations affecting the position of the boiler curve. This occurs because the curve, as presented, is determined from the mean temperature profile, the mean residence time, and (for nongaseous hazardous wastes) the time and temperature requirements to vaporize the waste.

6.5 COMPOSITE COMPOUND CURVES FOR SELECTED WASTE STREAMS -- RELATIVE INCINERABILITY

Tables 27 and 28 present physical and kinetic data for compounds associated with the chosen hazardous waste streams. The data were obtained from a limited literature search. As can be seen, there are large gaps in the available information and, furthermore, the data are often reported in a manner that is not directly applicable. For instance:

- Densities -- some values are for solids
- Heat capacities -- very few reported temperature dependencies
- Kinetic rate expressions
  - Pyrolysis data are usually for a specific bond cleavage as opposed to compound disappearance
  - Oxidation data rarely give oxygen concentration dependence. Most work has been conducted in air as opposed to 2 to 5 percent excess oxygen.

With the preceding deficiencies in mind, the predictions of waste stream destruction in Section 7 must be recognized as examples of the approach and not firm predictions of destructibility.

Our approach is to use conservative worst case characteristics in establishing a waste stream composite compound curve and comparing it to boiler curves. For the kinetic rate expression, the smallest Arrenhius pre-exponent (A) and largest energy of activation (E) are chosen from the available compound data on a given stream. This represents a very conservative approach in that very small frequency factors are rarely associated with very large activation energies. Where kinetic data are not

TABLE 25. CLASSES OF ORGANIC COMPOUNDS ASSOCIATED WITH PARTICULAR HAZARDOUS WASTE STREAMS

EPA hazardous waste number	Aromatics	Oxygenated aromatics	Chlorinated aromatics	Chlorinated aliphatics	Olefins	Unsaturated carbonyls	Polynuclear aromatics	Oxygenated aliphatics
F003	X							X
F004		X						
F005	X	X						X
K012						X		
K015			X					
K018			X	X	X			
K022	X	X					X	
K030			X	X	X			

TABLE 26. COMPOUNDS APPEARING IN SELECTED HAZARDOUS WASTE STREAMS

Stream	Components	
F003	Spent nonhalogenated solvents: xylene, ethyl benzene, cyclohexanone, acetone, ignitable solids (10 to 50 percent of original waste)	
F004	Spent nonhalogenated solvents: cresol, nitrobenzene, ignitable solids (10 to 50 percent of original waste)	
F005	Spent nonhalogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, pyridine, "still bottom residues" (10 to 50 percent of original waste)	
K012	Still bottoms from final purification of acrylonitrile	
	Acrolein	6 g/kg waste
	Acrylamide	6 g/kg waste
	Acrylonitrite	0.1 g/kg waste
K015	Still bottoms from the distillation of benzyl chloride	
	• By photochlorination	
	Benzal chloride	20 g/kg waste
	Trichlorobenzenes	5 g/kg waste
	Tetrachlorobenzene	5 g/kg waste
	Pentachlorobenzene	5 g/kg waste
	Hexachlorobenzene	5 g/kg waste
	• By catalytic chlorination	
	Benzal chloride	100 g/kg waste
	Chlorobenzene	10 g/kg waste
	Trichlorobenzenes	10 g/kg waste
K018	Heavy ends from ethyl chloride production	
	Ethyl chloride	3 g/kg waste
	1,2-dichloroethane	20 g/kg waste
	Trichloroethane	30 g/kg waste
	Hexachlorobutadiene	40 g/kg waste
	Hexachlorobenzene	40 g/kg waste

(continued)

TABLE 26. (continued)

Stream	Components	
K022	Distillation tars from phenol production by cumene process	
	Acetophenone	1.9 g/kg waste
	Phenol	0.75 g/kg waste
	Cumyl phenol	0.85 g/kg waste
	Other tars	50-100 g/kg waste
K030	Column bottoms or heavy ends from combined production of trichloroethylene and perchloroethylene	
	Hexachlorobutadiene	230 g/kg waste
	Hexachlorobenzene	20 g/kg waste
	Hexachloroethane	10 g/kg waste
	Tetrachloroethane	10 g/kg waste
	Ethylene chloride	10 g/kg waste
	Chlorobutadiene	10 g/kg waste

TABLE 27. PHYSICAL DATA FOR COMPOUNDS IN SELECTED HAZARDOUS WASTE STREAMS (REF. 45)

Hazardous waste number	Chemical compound	Melting point (°C)	Boiling point (°C)	Specific gravity (20°C)	Heat capacity (cal/g-°C)	ΔH°vap (cal/g)	Auto-ignition temperature (°K)	Remarks
F003	o-xylene	-25.0	144.0	0.880	0.411 (0.451)*	94.33		*30°C (39°C)
	m-xylene	-48.0	139.0	0.860	0.393+; 0.40++; (0.387)	93.44		+0°C ++9°-40°C (16°-35°C)
	p-xylene	13.0	138.0	0.861	0.383* 0.397+ (0.428)	92.54		*0°C +30°C (40.8°)
	Ethylbenzene	-95.0	136.0	0.867	0.392 (0.407)	87.75		0°C (30°C)
	Cyclohexanone	-45.0	155.0	0.947	0.431*			*15°-18°C
	Acetone	-95.35	56.2	0.7899	0.514-0.538	134.74	738	See K022
F004	o-cresol	31.0	191.0	1.0273	0.497*	115.62	832	*0°-20°C
	m-cresol	11.0	201.0	1.0336	0.551**	124.85	832	**21°-197°C
	p-cresol	35.0	202.0	1.0178		126.03	832	
	Nitrobenzene	5.7	210.9	1.205	0.358; 0.339; 0.330 (0.343); 0.394	79.08	756	10°C, 30°C, 50°-70°C (90°C), 120°C
F005	Toluene	-95.0	110.8	0.866	0.364; 0.534 (0.44)	101.83	809	10°C, 85°C, (12-99)
	Pyridene	-42	115.0	0.982	0.405; 0.431 (0.395)	107.36	816	20°C, 21°-108°C (0-20)
	Methylethyl ketone	-85.9	79.6	0.805	0.549	105.93	747	20°-78°C
	Carbon disulfide	-108.6	46.3	1.263		89.29	373	
K012	Acrolein	-87.7	52.5	0.841			507	
	Acrylamide		84.85				797	
	Acrylonitrile	-82	78-79	0.811			754	
K015A	Benzylchloride	-39	179	1.10	0.323			
	Trichlorobenzene	17-63.5	208.5-219	1.574			844	
	Tetrachlorobenzene	47-138	246-254	1.734				
	Pentachlorobenzene	86	277	1.834				
	Hexachlorobenzene	228	326	2.044		30.55		
K015B	Benzylchloride	-39	179	1.10	0.323			
	Chlorobenzene	-45.2	131	1.107		77.6	911	
	Trichlorobenzene	63.5	208.5				844	
K018	Ethylchloride	-139.0	13.0	0.917	0.426 (0.367)	92.9	792	-28° to +4°C (0°C)
	1,2-dichloethane	-35.3	83.7	1.256			686	
	Hexachlorobenzene	228.31	309.0	2.044		30.55		
	Trichloroethane	--	74.1	1.325	0.266		856, 955	20°C
	Hexachlorobutadiene						883	

(continued)

TABLE 27. (continued)

Hazardous waste number	Chemical compound	Melting point (°C)	Boiling point (°C)	Specific gravity (20°C)	Heat capacity (cal/g-°C)	ΔH°vap (cal/g)	Auto-ignition temperature (°K)	Remarks
K022	Acetone	-94.6	56.5	0.792	0.514*; 0.538**	105-130	738	*3°-22.4°C; **24.2°-49.4°C
	Phenol	42.0	181.4	1.07	0.561 (s)	126.41	988	
	Cumene	-96.9	152.5	0.862		89.77		
K030	Trichloroethylene	-73.0	87.2	1.466	0.223	57.24	683	20°C
	Hexachlorobenzene	228.0	309.0	2.044		30.55		
	Hexachloroethane	186.0	186.0	2.09	0.174 (s)	26.06		
	Ethyl chloride	-139.0	13.0	0.917	0.426 (0.367)	92.93	792	-28° to +4°C (0°C)
	Chloro-buta-1,3-diene	--	59.4	0.958				
	Chloro-buta-1,2-diene	--	88.0	0.991				

TABLE 28. KINETIC DATA FOR COMPOUNDS OCCURRING IN SELECTED HAZARDOUS WASTE STREAMS (REF. 45, 46, 54)

	Oxidation (in air)		Pyrolysis	
	A (sec^{-1})	E (kcal/g-mole)	A (sec^{-1})	E (kcal/g-mole)
		Aromatics		
Benzene	7.42×10^{21}	95.9		
Chlorobenzene				
Dichlorobenzene				
Trichlorobenzene				
Tetrachlorobenzene				
Pentachlorobenzene				
Hexachlorobenzene	1.9×10^{16}	72.6		
Ethylbenzene			10^{13}	63
m-xylene			4.2×10^{12}	77.5
p-xylene			4.8×10^{12}	76
o xylene			4.8×10^{12}	75
Toluene	2.28×10^{13}	56.5	2.1×10^{12}	77.5
Methyl naphthalene			1.5×10^{13}	73.5
Propylbenzene			3.2×10^{13}	57.5
Bromobenzene			2×10^{13}	70.9
Benzylbromide			10^{13}	50.5
Biphenyl	3.55×10^{16}	70.7		
Tetrachloro biphenyl	6.8×10^{16}	77		
Pentachloro biphenyl	1.1×10^{16}	70.0	7.44×10^{9}	53.6
Decachloro biphenyl	3.46×10^{12}	55		
Hexachloro biphenyl	2.7×10^{16}	71		
		Aliphatics		
Methane	1.68×10^{11}	52.1		
Ethane	5.65×10^{14}	63.6	2×10^{17}	84
Propane	5.25×10^{19}	85.2		
Ethyl chloride			4×10^{14}	60.8
1,1 dichloroethane			1.3×10^{12}	49.5
1,2 dichloroethane	4.82×10^{11}	45.6	10^{13}	70

(continued)

TABLE 28. (continued)

	Oxidation (in air)		Pyrolysis	
	A (sec^{-1})	E (kcal/g-mole)	A (sec^{-1})	E (kcal/g-mole)
	Aliphatics (continued)			
1,1,1 Trichloroethane			3.2×10^{12}	47.9
Propyl chloride			2.8×10^{13}	55.0
Isopropyl chloride			2.5×10^{13}	50.5
1,2 Dichloropropane			6.3×10^{13}	54.9
Propyl bromide			4×10^{13}	47.7
Isopropyl bromide			10^{13}	50.7
	Oliphenics			
Ethylene	1.37×10^{12}	50.8		
Propylene	4.63×10^{8}	34.2		
Butene	3.74×10^{14}	58.2	5×10^{12}	63
Vinyl chloride	3.57×10^{14}	63.3		
Vinyl bromide			5×10^{12}	47.5
	Miscellaneous			
Ethanol	5.37×10^{11}	48.1		
t-Butanol			4.8×10^{14}	66
t-Amyl Alcohol			3.2×10^{13}	60
Ethyl acetate			3.2×10^{12}	47
Isopropyl acetate			10^{13}	45.0
t-Butyl acetate			2.2×10^{13}	40.5
Ethyl acrylate	2.19×10^{12}	46		
Acrylonitrile	2.18×10^{12}	52.1		
Acrolein	3.3×10^{10}	35.9		
Acetic anhyride	10^{12}	34.5		

available, an arbitrary A of 10^{10} and an E of 70 kcal/mole has been used. (As noted above, high E values (>70) and low A values (>10^{10}) do not occur with the same compound.)

The composite compound parameters for selected waste streams is given in Table 29. Figure 23 plots the gas phase time-temperature requirement for each stream where pyrolytic data are available. Pyrolytic data are used because they are the most conservative, and the only oxidation data are for air (20-percent oxygen), as opposed to 2 to 5 percent oxygen.

6.6 AUTOIGNITION TEMPERATURES AND DESTRUCTIBILITY

Autoignition temperatures are more widely available than kinetic destruction data. Autoignition temperature has been shown to be a good predictor of relative combustibility for 15 compounds (Ref. 46). There is currently insufficient data on oxidative destruction of compounds to verify this predictor for other compounds.

There is a much wider data base available on pyrolytic destruction. However, pyrolytic destruction proceeds by mechanisms different from oxidative destruction. Even though oxidative destruction can be orders of magnitude faster than pyrolytic destruction, the relative rates between a series of compounds can be reversed. For example, the rate constants for oxidation of ethane and 1,2-dichloroethane are approximately 7.1 and 52 sec^{-1} at 1,000K. For pyrolysis, the relative order is reversed, being about 0.09 and 0.005 sec^{-1}.

With the previous caveats in mind, a table of the relative destructibility of compounds, based on the K.C. Lee autoignition temperature predictor (Ref. 46) has been prepared (Table 30). A second table has been prepared (Table 31), grouping compounds into structural classes and indicating the limiting compound (most refractory) for destruction.

TABLE 29. COMPOSITE COMPOUND PARAMETERS[a] BY WASTE STREAM

	Melting point (°C)	Boiling point (°C)	Specific gravity[b]	Heat capacity (cal/g-°C)	ΔH°_{vap} (cal/g)	A (sec-1)	E (kcal/g-mole)	Mode
F003	13	155	0.947	0.538	134.7	5×10^{12}	78	Pyrolysis
F004	35	211	1.205	0.551	126	(10^{10})[c]	(70)[c]	(Pyrolysis)
F005	-42	115	1.263	0.549	106	2.1×10^{12}	77.5	Pyrolysis
K012	-82	85	0.841	(0.6)	(140)	3.3×10^{10}	52.1	Oxidation
K015	228	326	1.834[b]	0.323	77.6	1.9×10^{16}	72.6	Oxidation
K018	228	326	1.834	0.426	91.3	3.2×10^{12}	70	Pyrolysis
K022	42	181	1.07[b]	0.561	126	(10^{10})[c]	(70)[c]	(Pyrolysis)
K030	228	326	2.09[b]	0.426	92.9	10^{13}	70	Pyrolysis

[a] Values in parentheses are arbitrary.
[b] Solid density.
[c] Guess.

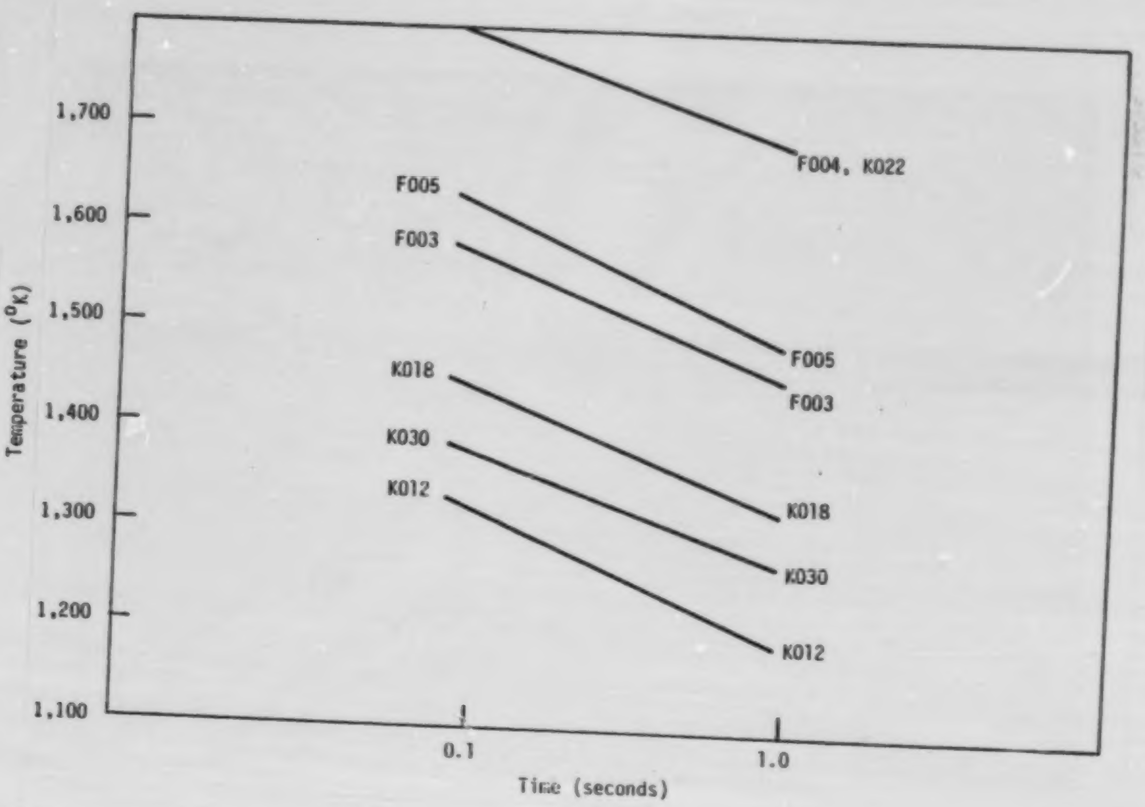

Figure 23. Plots of time-temperature relationships required for 99.99-percent destruction of selected hazardous waste streams (assuming destruction is by the conservative pyrolysis mode and using the lowest A and highest E values for compounds in the stream).

TABLE 30. ORDER OF INCREASING DESTRUCTIBILITY BY TEMPERATURE REQUIRED FOR 99.99-PERCENT DESTRUCTION AT 1-SECOND RESIDENCE TIME

Order	Compound	T (°F) needed at 1 sec	Destruction rate data
1	Methyl chloride	1,550	
2	Methane	1,535	X
3	Phenol	1,484	
4	Methylene chloride	1,466	
5	Pyridine	1,455	
6	Chlorobenzene	1,413	
7	Dichlorobenzene	1,408	
8	Hexachlorobenzene	1,405	X
9	Ethane	1,401	X
10	Vinyl chloride	1,374	X
11	Ethyl chloride	1,358	
12	Benzene	1,358	X
13	Cresol	1,331	
14	Ethylene	1,329	X
15	Toluene	1,327	X
16	Nitrobenzene	1,327	
17	Hexa chlorobutadiene	1,325	
18	Trichlorobenzene	1,320	
19	Vinylidene chloride	1,313	
20	Acetophenol	1,310	
21	Propane	1,305	X
22	1,2,2-trichloro-1,1,2-trifluoroethane	1,277	
23	Dichloropropane	1,266	
24	Trichloroethane	1,260	
25	Phthalic anhydride	1,240	
26	Isobutanol	1,229	
27	Trichloroethylene	1,222	
28	Naphthalene	1,221	
29	Methyl ethyl ketone	1,213	
30	Dichloroethane	1,212	X
31	Epichlorohydrin	1,143	
32	Maleic anhydride	1,123	
33	Bis(2-chloroethyl) ether	1,115	
34	Methyl isobutyl ketone	1,109	
35	Trichloropropane	1,060	
36	Benzotrichloride	982	
37	Carbon disulfide	751	

TABLE 31. WORST CASE COMPOUND FOR DESTRUCTION BY STRUCTURAL CLASS

Compound	Limiting (more refractory) compound with data	Reasoning
Methane	Methane	Data
Methyl chloride	Methane	UCT
Methylene chloride	Methane	UCT
Chloroform	Methane	Analogy
Carbon tetrachloride	Methane	Analogy
Carbon disulfide	Dichloropropane	UCT
Ethane	Ethane	Data
Ethyl chloride	Vinyl chloride	UCT
Dichloroethanes	Dichloroethanes	Data
Trichloroethanes	Propane	UCT
Tetrachloroethanes	Propane	Analogy
Pentachloroethanes	Propane	Analogy
Hexachloroethanes	Propane	Analogy
Trichlorotrifluoroethane	Propane	Analogy
Ethylene	Ethylene	Data
Vinyl chloride	Vinyl chloride	Data
Vinylidine chloride	Vinyl chloride	UCT
Trichloroethylene	Propane	UCT
Perchloroethylene	Propane	Analogy
Bis(chloromethyl)ether	Dichloroethanes	Analogy with Bis(2-chloromethyl)ether
Propane	Propane	Data
Chloropropane	Propane	TP
Dichloropropane	Propane	UCT
Trichloropropane	Dichloroethanes	UCT
Dichloropropanols	Propane	Analogy
Epichlorohydrin	Dichloroethanes	UCT
Isobutanol	Propane	UCT
Chlorobutadiene	Toluene	Analogy
Hexachlorobutadiene	Toluene	UCT
Maleic Anhydride	Dichloroethanes	UCT
Bis(2-chloroethyl)ether	Dichloroethanes	UCT

(continued)

UCT -- Union Carbide predicted temperature
TP -- Thermal pyrolysis data
Analogy -- Structural correlation and speculation

TABLE 31. (continued)

Compound	Limiting (more refractory) compound with data	Reasoning
Methyl ethyl ketone	Dichloroethanes	UCT
Methyl isobutyl ketone	Dichloroethanes	UCT
Benzene	Benzene	Data
Chlorobenzene	Hexachlorobenzene	UCT
Dichlorobenzene	Hexachlorobenzene	UCT
Trichlorobenzene	Hexachlorobenzene	UCT
Tetrachlorobenzene	Hexachlorobenzene	Analogy
Pentachlorobenzene	Hexachlorobenzene	Analogy
Hexachlorobenzene	Hexachlorobenzene	Data
Pyridine	Methane	UCT
Nitrobenzene	Toluene	UCT
Phenol	Methane	UCT
Chlorophenol	Methane	Analogy
Dichlorophenol	Methane	Analogy
Trichlorophenol	Methane	Analogy
Tetrachlorophenol	Methane	Analogy
Pentachlorophenol	Methane	Analogy
Nitrophenols	Methane	Analogy
Toluene	Toluene	Data
Benzalchloride	Toluene	Analogy
Benzotrichloride	Dichlorethane	UCT
Cresols	Benzene	UCT
Cresylic acid	Benzene	Analogy
Nitrocresols	Benzene	Analogy
Dinitrocresols	Benzene	Analogy
Acetophenone	Toluene	UCT
Phthatic anhydride	Propane	UCT
Dimethyl phenols	Methane	Analogy
Cumyl phenol	Methane	Analogy
Naphthalene	Propane	UCT
Naphthoquinone	Propane	Analogy

UCT -- Union Carbide predicted temperature
TP -- Thermal pyrolysis data
Analogy -- Structural correlation and speculation

SECTION 7

USE OF INDUSTRIAL BOILERS TO BURN HAZARDOUS WASTE

Boiler and waste characteristics must be compared to determine the suitability of a boiler to burn hazardous wastes. The boiler characteristics developed in Section 5 give the bulk temperature and mean residence time profiles for selected industrial boilers. The destruction curves developed in Section 6 give the time-temperature requirements for the destruction of a given waste. By overlaying the results of Sections 5 and 6, an evaluation can be made of which boilers are suitable for cofiring hazardous wastes and which wastes are amenable to cofiring.

The purpose of this section is to apply the predictive model of Section 6 to selected hazardous waste streams and boiler conditions. The approach is to:

- Present boiler parameters
- Determine effects of hazardous waste characteristics on boiler time-above-temperature curves
- Verify the assumption that hazardous waste constituents are in the gas phase hazardous waste at t_m
- Calculate boiler time above temperature curves
- Compare compound and boiler curves
- Make destructibility prediction

7.1 BOILER PARAMETERS

The boiler parameters for seven boiler classes and operational paths are given in Table 32. This table is derived from the boiler time-temperature profiles of Section 5, and curve fitting using the approximation formulas of Section 6.2.3. To reiterate, the curve fitting formula for temperature rise over the time interval t_o to t_m (the temperature rise portion) is:

$$T = a + b \ln t \qquad (7\text{-}1)$$

where t_o = 0.001 sec, T_o = 400K, t ranges from t_o to t_m and T ranges from T_o to T_m. For the temperature fall portion, the formula is:

$$T = c \exp(Dt) \qquad (7\text{-}2)$$

where t ranges from t_m to t_e, and T ranges from T_m to T_e. Intermediate points for the curve fit were obtained by manual reading of the

TABLE 32. BOILER TEMPERATURE PARAMETERS

Boiler	a	b	c	D	t_m (sec)	T_m (°K)	t_e (sec)	T_e (°K)
G: 58.6 MW (200 million Btu/hr) Pulverized-coal-fired watertube								
Full load -- mean path	2,296	274	1,993	-0.15	0.20	1,790	1.73	1,435
-- fast path	2,335	280	1,726	-0.21	0.10	1,690	0.88	1,435
Half load -- mean path	1,922	205	1,759	-0.09	0.39	1,585	3.5	1,195
-- fast path	1,815	205	1,526	-0.14	0.20	1,485	1.8	1,195
F: 44 MW (150 million Btu/hr) Spreader-stoker watertube								
Full load -- mean path	1,817	203	1,865	-0.22	0.59	1,620	1.57	1,325
-- fast path	1,756	196	1,653	-0.28	0.30	1,520	0.79	1,325
Half load -- mean path	1,393	143	1,627	-0.12	0.75	1,315	3.2	1,080
-- fast path	1,348	137	1,260	-0.10	0.38	1,215	1.6	1,080
E: 44 MW (150 million Btu/hr) Residual-oil-fired packaged watertube								
Full load -- mean path	2,252	266	1,876	-0.40	0.19	1,700	0.83	1,295
-- fast path	2,200	261	1,709	-0.66	0.10	1,600	0.42	1,295
Half load -- mean path	1,842	208	1,689	-0.27	0.41	1,490	1.85	1,045
-- fast path	1,679	185	1,511	-0.40	0.21	1,390	0.93	1,045
D: 4.4 MW (150 million Btu/hr) Distillate-oil-fired packaged watertube								
Full load -- mean path	2,269	269	1,921	-0.38	0.20	1,715	0.84	1,340
-- fast path	2,223	264	1,712	-0.58	0.10	1,615	0.42	1,340
Half load -- mean path	1,824	205	1,725	-0.25	0.41	1,505	1.81	1,085
-- fast path	1,698	188	1,518	-0.37	0.21	1,405	0.91	1,085
C: 4.4 MW (150 million Btu/hr) Natural-gas-fired packaged watertube								
Full load -- mean path	2,122	250	2,145	-0.41	0.35	1,815	0.83	1,475
-- fast path	2,149	253	1,920	-0.63	0.18	1,715	0.42	1,475
Half load -- mean path	1,781	194	1,910	-0.26	0.72	1,575	1.78	1,210
-- fast path	1,662	183	1,687	-0.37	0.36	1,475	0.89	1,210

(continued)

TABLE 32. (continued)

Boiler	a	b	c	D	t_m (sec)	T_m (°K)	t_e (sec)	T_e (°K)
B: 4.4 MW (15 million Btu/hr) Distillate-oil-fired packaged firetube								
Full load -- mean path	2,357	285	2,011	-1.14	0.12	1,710	0.25	1,490
-- fast path	2,441	296	1,721	-1.11	0.06	1,610	0.13	1,490
Half load -- mean path	1,850	214	1,862	-0.68	0.26	1,515	0.55	1,235
-- fast path	1,840	209	1,592	-0.91	0.13	1,415	0.18	1,235
A: 4.4 MW (15 million Btu/hr) Natural-gas-fired packaged firetube								
Full load -- mean path	2,756	341	2,175	-1.19	0.11	1,815	0.25	1,600
-- fast path	2,619	321	1,820	-0.99	0.06	1,715	0.13	1,600
Half load -- mean path	2,193	261	1,960	-0.69	0.15	1,630	0.52	1,335
-- fast path	2,181	258	1,620	-0.72	0.08	1,530	0.27	1,335

time-temperature profile plots in Section 5. The curve constants (a, b, c, D) were calculated using a least squares curve fit program on a hand-held programmable calculator. The regression fit (r^2) ranged from 0.94 to 1.0. Reported time and temperature values (T_m and T_e in Table 32) are taken directly from the zonal heat balance calculations and are not those calculated from the curve fit parameters.

7.2 EFFECTS OF STREAM PHYSICAL PROPERTIES ON BOILER TIME-ABOVE-TEMPERATURE CURVES

In the development of the model in Section 6, it was assumed that all hazardous waste constituents were in the vapor phase at time t_m. The validity of this assumption is dependent on the physical properties of the waste stream and the droplet size of the atomized waste. This assumption will now be verified for various streams and boiler conditions.

The method of verification is to calculate the time necessary to reach full volatilization under given boiler conditions. The approach is again conservative. The material will first be raised from some ambient starting temperature to its boiling point, and then vaporized. (In reality, there will be extensive surface boiling before the bulk of the material reaches its boiling point). The two following subsections develop the equations for these calculations.

7.2.1 Initial Heating Time

The initial heating time, t_h, is the time necessary to heat the material to its boiling point (assuming it is a liquid). The amount of heat required is:

$$Q = m \int_{T_{am}}^{T_{bp}} C_p(T)\, dT \tag{7-3}$$

where

Q = heat required (cal)

m = mass of hazardous waste (g)

$C_p(T)$ = heat capacity of the hazardous waste as a function of its temperature (cal/g-K)

T_{am} = injection temperature of material

T_{bp} = boiling point of hazardous waste

The rate of heating is:

$$\frac{dQ}{dt} = hA \left[T_b (t) - T_h (t) \right] \qquad (7\text{-}4)$$

where

h = convective heat transfer coefficent of the hazardous waste $(\mathrm{cal/cm^2 \cdot S \cdot {}^\circ K})$

A = surface area of hazardous waste droplet $(\mathrm{cm^2})$

$T_b(t)$ = boiler ambient temperature at time t (°K)

$T_h(t)$ = bulk hazardous waste droplet temperature at time t (°K)

The free convective heat transfer coefficient is chosen as the most conservative rate of heat transfer within the liquid hazardous waste.

Combining and rearranging Equations (7-3) and (7-4):

$$\int_{t_o}^{t_h} \Delta T \, dt = \frac{m}{hA} \int_{T_{am}}^{T_{bp}} C_p(T) \, dT \sim \frac{m\overline{C}_p}{hA} (T_{bp} - T_{am}) \qquad (7\text{-}5)$$

where $\Delta T = T_b(t) - T_h(t)$, and $\overline{C}_p$ is the average waste heat capacity over the temperature range T_{am} to T_{bp}.

From Section 5, for the temperature rise portion of the boiler, the time-temperature relationship in the boiler is approximated by:

$$T_b(t) = a + b \ln t \qquad (7\text{-}6)$$

The difference, ΔT, between the boiler temperature and the waste temperature is:

$$\Delta T = T_b(t) - T_h(t) \qquad (7\text{-}7)$$

If at t_o, the quantity $\Delta T = 0$ (conservative, since waste temperature will be be below boiler temperature at its injection point), then it can be shown that:

$$\Delta T = \frac{t}{t_h} (a + b \ln t_h - T_{bp}) \qquad (7\text{-}8)$$

Integrating the right side of this equation with respect to time, (dt), over the interval t_o to t_h results in:

$$\int_{t_o}^{t_h} \Delta T \, dt = \frac{t^2}{t_h} (a+b \ln t_h - t_{bp}) \Big|_{t_o}^{t_h} \qquad (7\text{-}9)$$

Inserting the right side of Equation (7-9) into Equation (7-5) and solving for Δt_h gives:

$$t_h (a + b \ln t_h - T_{bp}) = \frac{m\bar{C}_p}{hA} (T_{bp} - T_{am}) \qquad (7\text{-}10)$$

where t_h = time to heat the material (sec) to its boiling point.

Assuming spherical droplets, the mass (m) and surface area (A) are:

$$m = \frac{\rho 4\pi \, r_o^3}{3}$$

and

$$A = 4\pi \, r_o^2$$

respectively, where

ρ = density of material (g/cm^3)

r_o = initial droplet radius (cm)

Replacing in Equation (7-10):

$$t_h (a + b \ln \, t_h - T_{bp}) = \frac{\rho r_o}{3h} \, \bar{C}_p (T_{bp} - T_{am}) \qquad (7\text{-}11)$$

7.2.2 Volatilization Time

The total amount of heat Q required to vaporize a droplet of hazardous waste (when it is at its boiling point) is just the heat of vaporization multiplied by the mass. That is:

$$Q = \frac{\rho 4\pi\ r_o}{3}\ \Delta H_{vap} \qquad (7\text{-}12)$$

The rate of heat transfer is:

$$\frac{dQ}{dt} = hA\ \Delta T(t) \qquad (7\text{-}13)$$

Taking the derivative of Equation (7-12) with respect to r and equating:

$$\frac{dQ}{dt} = h\ (4\pi r^2)\ \ \Delta T(t) = \frac{4\pi\rho}{3}\ \Delta H_{vap} \left(3\ r^2 \frac{dr}{dt}\right) \qquad (7\text{-}14)$$

Simplifying, canceling terms, and integrating:

$$\int_{t_h}^{t_v} \Delta T(t)\ dt = \frac{\rho \Delta H_{vap}}{h} \int_{o}^{r_o} dr \qquad (7\text{-}15)$$

Remembering that $\Delta T(t) = T_B(t) - T_h(t)$ and at this point $T_h(t) = T_{bp}$, then $\Delta T(t) = a + b \ln t - T_{bp}$ and the integral is evaluated as:

$$(a - b - T_{bp})\ \Delta t_v + b\ (t_v \ln t_v - t_h \ln t_h) = \frac{\rho r_o\ \Delta H_{vap}}{h} \qquad (7\text{-}16)$$

where $\Delta t_v = t_v - t_h$, and it is assumed that complete volatization occurs before the droplet passes the peak temperature of the boiler profile.

To determine t_v, Δt_v must be added to t_h and:

$$t_v \left[a + b \ln t_v - (b + T_{bp})\right] = \frac{\rho r_o}{h} \left[\Delta H_{vap} + \frac{\bar{C}_p}{3} (T_{bp} - T_{am})\right] - bt_h \qquad (7\text{-}17)$$

If $t_v > t_m$ (time to maximum temperature), a slightly different form of the equation is used. This form is:

$$t_v = \frac{1}{D} \ln \left[\frac{M + T_m}{c} \right] \tag{7-18}$$

where

$$M = D \left\{ \frac{\rho r_o}{h} \left[\Delta H_{vap} + \frac{\bar{C}_p}{3} (T_{bp} - T_{am}) \right] - t_m (T_m - T_{bp}) - b(t_h - t_m) \right\}$$

and c and D are boiler temperature profile constants for the temperature fall portion of the boiler profile.

7.3 CALCULATION OF TIME TO VAPORIZATION AND COMPARISON TO BOILER MAXIMUM TEMPERATURE

Hazardous waste "composite compound" data were presented in Table 29. Values needed for calculation of time to vaporization are density (ρ), boiling point, heat capacity (C_p), and heat of vaporization (ΔH_{vap}). Times to vaporization are increasing functions of these parameters. Therefore, the largest of each parameter is taken from the stream data set to form the properties of the "composite compound."

Vaporization times for two droplet diameters, 80 µm and 200 µm are calculated. The 80-µm droplet represents the mass mean diameter of most fuel (assumed to be comparable to waste) droplets, while less than 1 percent are above 200 µm. The time to vaporization for the 200 µm droplet was calculated for all streams under one boiler condition (pulverized coal, full load, mean path). For that stream with the longest t_v (K030), calculations were performed for all boilers.

The time of heating and time of vaporization values were calculated by iterative closure of the equations relating time and total heat input (Equations (7-11) and (7-16)). The two values were found independently and then summed. The results are tabulated in Table 33.

As was assumed, the time to vaporization was less than t_m in all but one case (200-µm droplet under full-load, fast-path conditions in a pulverized-coal boiler). Firetube boilers will probably not meet the assumption for fast path conditions, nor will the distillate-oil-fired watertube boilers under full-load, fast-path conditions. Conversely, it is not probable that the largest droplets will take the fastest path.

TABLE 33. TIME TO VAPORIZATION (SEC) FOR SELECTED HAZARDOUS WASTE STREAMS UNDER VARIOUS BOILER CONDITIONS (80 μm DIAMETER DROPLETS)

Boiler	F003	F005	K012	K018	K030		Boiler t_m
					80 μm	200 μm	
G: 58.6 MW (200 million Btu/hr) Pulverized-coal-fired watertube							
Full load -- mean path	0.03/0.06[a]	0.03/0.07[a]	0.03/0.06[a]	0.05/0.10[a]	0.05	0.11	0.20
Full load -- fast path	0.03/0.07	0.03/0.07	0.03/0.06	0.05/0.09	0.05	0.11	0.10
Half load -- mean path	0.04	0.04	0.04	0.06	0.07	0.14	0.39
F: 44 MW (150 million Btu/hr) Spreader-stoker watertube							
Full load -- mean path	0.04	0.04	0.04	0.06	0.07	0.14	0.59
Half load -- mean path	0.06	0.05	0.05	0.09	0.10	0.20	0.75
E: 44 MW (150 million Btu/hr) Residual-oil-fired packaged watertube							
Full load -- mean path	0.03	0.03	0.03	0.05	0.05	0.11	0.19
Half load -- mean path	0.04	0.04	0.04	0.06	0.07	0.14	0.41
D: 44 MW (150 million Btu/hr) Distillate-oil-fired packaged watertube							
Full load -- mean path	0.03	0.03	0.03	0.05	0.05	0.11	0.20
Half load -- mean path	0.04	0.04	0.04	0.06	0.07	0.11	0.41
C: 44 MW (150 million Btu/hr) Natural-gas-fired packaged watertube							
Full load -- mean path	0.04	0.04	0.03	0.05	0.06	0.12	0.35
Half load -- mean path	0.04	0.04	0.04	0.06	0.07	0.14	0.72
B: 4.4 MW (15 million Btu/hr) Distillate-oil-fired packaged firetube							
Full load -- mean path	0.03	0.03	0.03	0.05	0.05	0.10	0.12
Half load -- mean path	0.04	0.04	0.04	0.06	0.07	0.14	0.26
A: 4.4 MW (15 million Btu/hr) Natural-gas-fired packaged firetube							
Full load -- mean path	0.03	0.03	0.03	0.04	0.04	0.09	0.11
Half load -- mean path	0.04	0.04	0.03	0.05	0.06	0.11	0.15

[a] For 200 μm diameter droplets

7.4 BOILER PARAMETERS AND DESTRUCTIBILITY (MOST CONSERVATIVE)

The boiler parameters needed for application of the model are given in Table 32. The most conservative approach to predicting boiler applicability will use the time difference $t_e - t_m$ and the exit temperature T_e (see Section 6.2.2). For a given waste stream, the pyrolysis data are used because they are more conservative than oxidation data, and the available oxidation data were obtained using air containing 20 percent oxygen as opposed to 2 to 5 percent oxygen, which more closely approximates actual conditions in boilers.

A model boiler example with five hypothetical compounds is shown in Figure 24. The boiler zone is generated from the following four data points (the assumption is made that the material is in gas phase at t_m; this has been verified in Section 7.3):

- The mean elapsed time the material is above exit temperature under full-load conditions
- The shortest elapsed time the material is above exit temperature at full-load
- The mean elapsed time the material is above exit temperature under half-load conditions
- The shortest elapsed time at half-load conditions

The area thus inscribed is called the boiler kinetic operational zone (BKOZ) above exit temperature. The points within the BKOZ represent the amount of time the gas is above the exit temperature, and the exit temperatures that can be obtained for a boiler operating between full and half load. These represent the range of thermodynamic points for calculating destruction efficiencies. If the time-temperature curve for 99.99-percent destruction of a given compound is overlayed on the BKOZ plot, the following two conclusions can be reached:

- Any compound whose kinetic curve lies above the BKOZ will never reach 99.99-percent destruction by most conservative estimates (e.g., compound A; Figure 24)
- Any compound whose plot lies below the BKOZ will always achieve 99.99-percent destruction under the given boiler conditions (e.g., compound E; Figure 24)

A third conclusion can be made that any compound whose plot lies completely beneath the upper bound line (T_e at full-load and 0.5 t_e to t_e at full-load) will always achieve 99.99-percent destruction under full-load conditions (e.g., compounds C, D, and E; Figure 24).

A corollary is that any compound whose plot lies completely above the lower bound line (T_e at half load and 0.5 t_e to t_e at half load) will not reach 99.99-percent destruction at half load conditions (e.g., compounds A, B, and C; Figure 24), if one were to rely on exit temperature alone for the destruction.

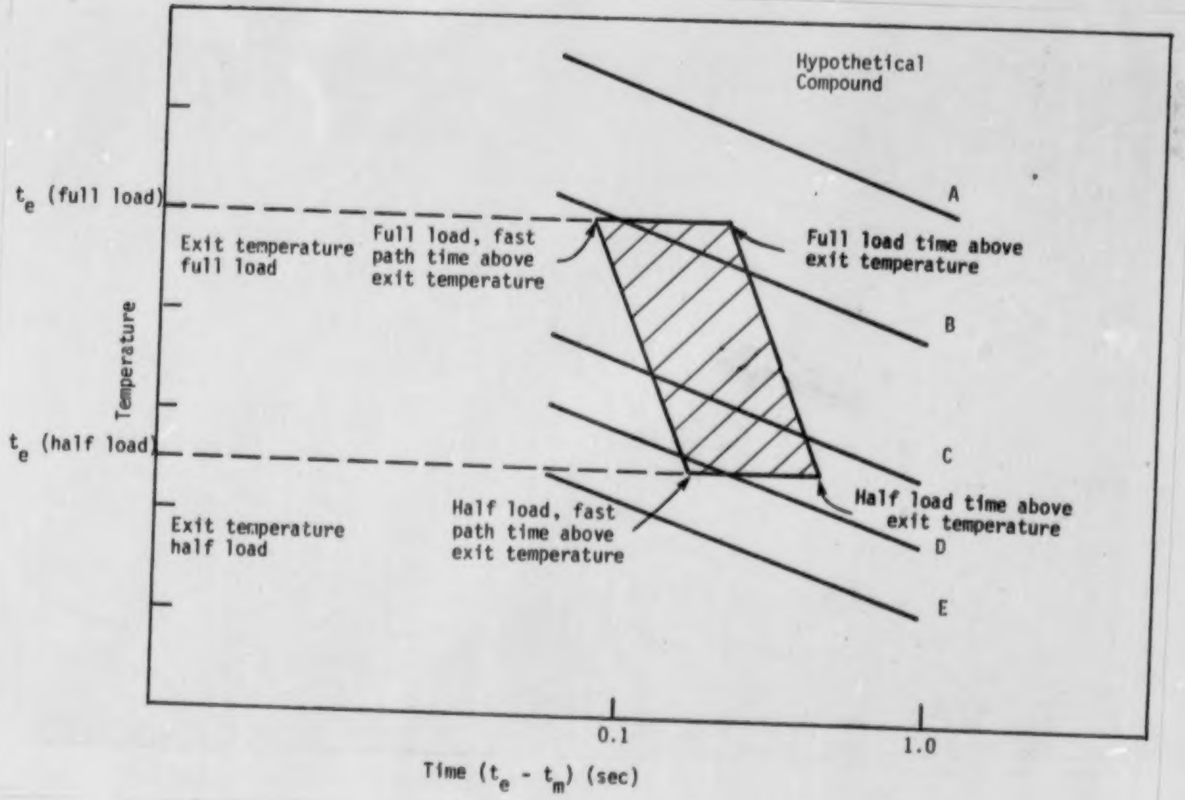

Figure 24. Example of overlaying compound curve and boiler curve -- most conservative case.

Figures 25 through 27 illustrate this approach for seven hazardous waste streams and seven types of boilers. The results are tabulated in Table 34. To reiterate these predictions are based on:

- The assumption that all material is in the gaseous state at t_m in the boiler
- Incomplete thermodynamic data
- No attempt to predict products of incomplete combustion (PIC's)
- No attempt to predict synergistic effects

Conversely, the kinetic data are for pyrolysis (which is much slower than oxidation) and the model does not account for destruction at temperatures above boiler exit temperatures.

In summary, this section predicts that:

- Stream K012 can be destroyed in all boilers studied
- Streams K018 and K030 can be destroyed in most of the boilers studied

7.5 EXTENDED APPROXIMATION TO DESTRUCTIBILITY

In this section, an extended BKOZ is developed to account for the higher destruction rates achieved at temperatures above the boiler exit temperature. The extension of the BKOZ is straightforward, but requires some care in interpretation. The problem is that the kinetic curves are not truly linear over more than one to two orders of magnitude in time, but tend to break upward at shorter times. Furthermore, essentially NO kinetic data exist for times shorter than 0.1 second.

Recall that in Section 6.2.2 a boiler time above temperature curve was developed. By constructing such curves from two points of the most conservative BKOZ, the extended BKOZ is generated. The two points of interest are the upper right (full load, mean path) and lower left (half load, fast path). An example is shown in Figure 28.

It is seen immediately that whereas under most conservative estimates it was questionable whether compound B would reach 99.99-percent destruction efficiency under full load, the kinetic plot falls below the full load, fast path curve and the waste is, indeed, predicted to be destructible. The same argument for half load conditions holds for compound D. Furthermore, it is apparent that compound C, predicted not to be destructible to 99.99-percent efficiency under half load conditions, can be destroyed.

The extended BKOZ for each boiler type under study is plotted in Figures 29 through 35. The appropriate hazardous waste stream kinetic curves are overlayed and a summary of the results (for the extended case) is given in Table 35.

TABLE 34. APPLICABILITY OF VARIOUS BOILERS TO THE GAS PHASE PYROLYSIS OF GIVEN STREAMS -- MOST CONSERVATIVE ESTIMATE (USING TIME ABOVE EXIT TEMPERATURE)

	Hazardous waste number						
Boiler	F003	F004	F005	K012	K018	K022	K030
G: 58.6 MW (200 million Btu/hr) Pulverized-coal-fired watertube							
Full load	X	N	N	A	A	N	A
Half load	N	N	N	A	N	N	P
F: 44 MW (150 million Btu/hr) Spreader-stoker-fired watertube							
Full load	N	N	N	A	N	N	A
Half load	N	N	N	P	N	N	P
E: 44 MW (150 million Btu/hr) Residential-oil-fired packaged watertube							
Full load	N	N	N	A	N	N	N
Half load	N	N	N	P	N	N	N
D: 44 MW (150 million Btu/hr) Distillate-oil-fired packaged watertube							
Full load	N	N	N	A	N	N	A
Half load	N	N	N	P	P	N	P
C: 44 MW (150 million Btu/hr) natural-gas-fired packaged watertube							
Full load	N	N	N	A	A	N	A
Half load	N	N	N	P	P	N	P

(continued)

TABLE 33. (continued)

	Hazardous waste number						
Boiler	F003	F004	F005	K012	K018	K022	K030
B: 4.4 MW (15 million Btu/hr) Distillate-oil-fired packaged f/retube							
Full load	N	N	N	A	A	N	A
Half load	N	N	N	X	P	N	P
A: 4.4 MW (15 million Btu/hr) Natural gas-fired packaged firetube							
Full load	X	N	N	A	A	N	A
Half load	N	N	N	A	P	N	X

A -- Applicable
P -- Probably applicable under conditions between full load and half load
X -- Marginally applicable (composite compound line passes below mean path, but above fast path)
N -- Not applicable (composite compound line is above mean path)

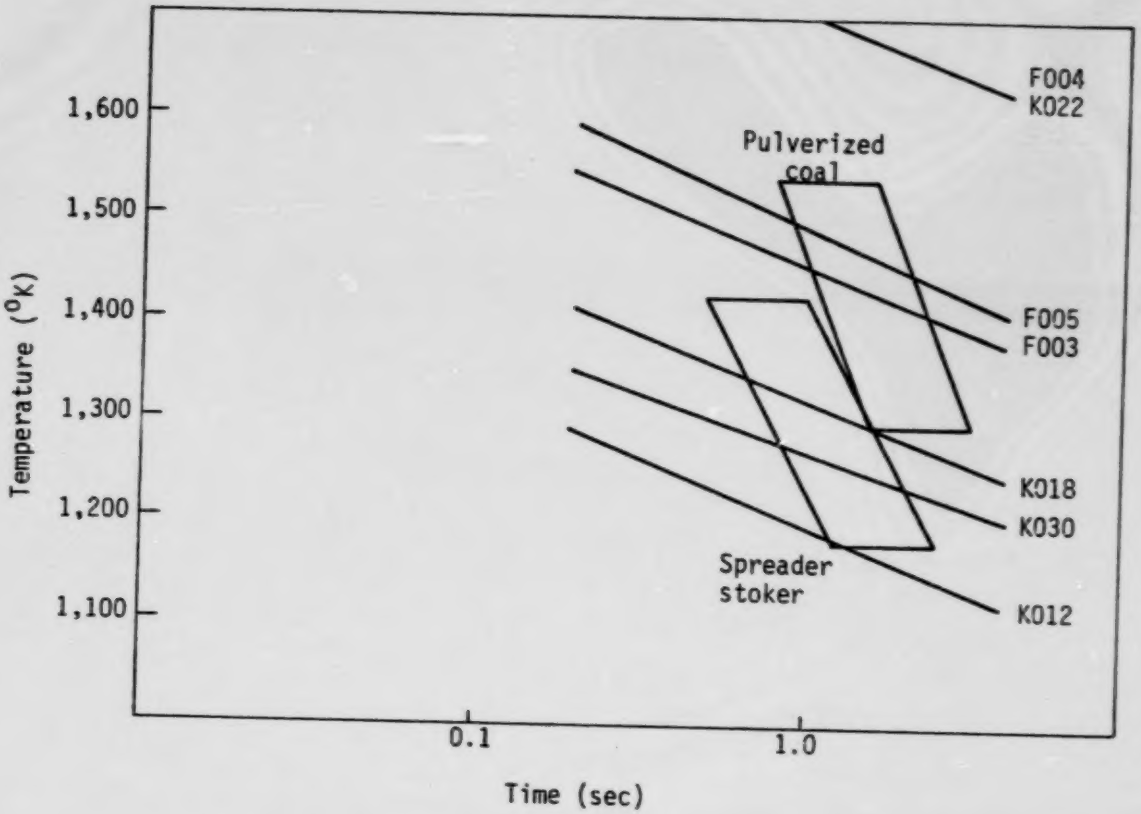

Figure 25. Stream destructibility predictions for pulverized-coal and spreader-stoker boilers.

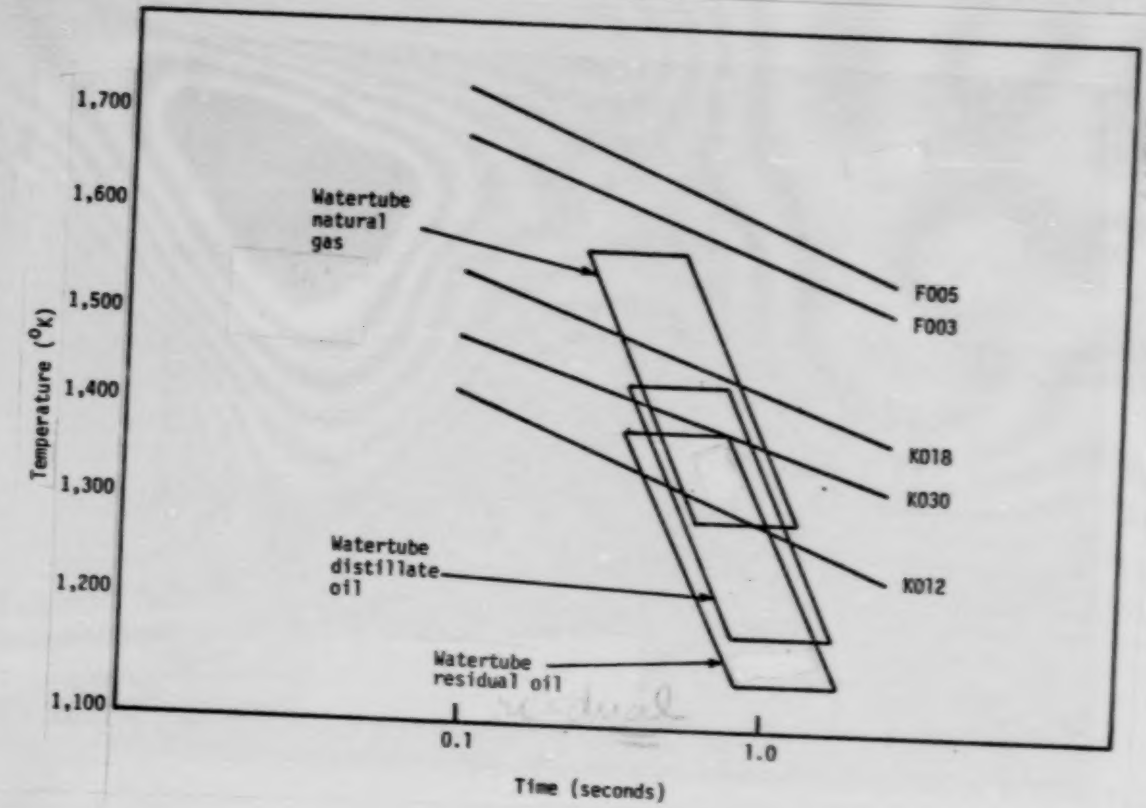

Figure 26. Stream destructibility predictions for watertube boilers.

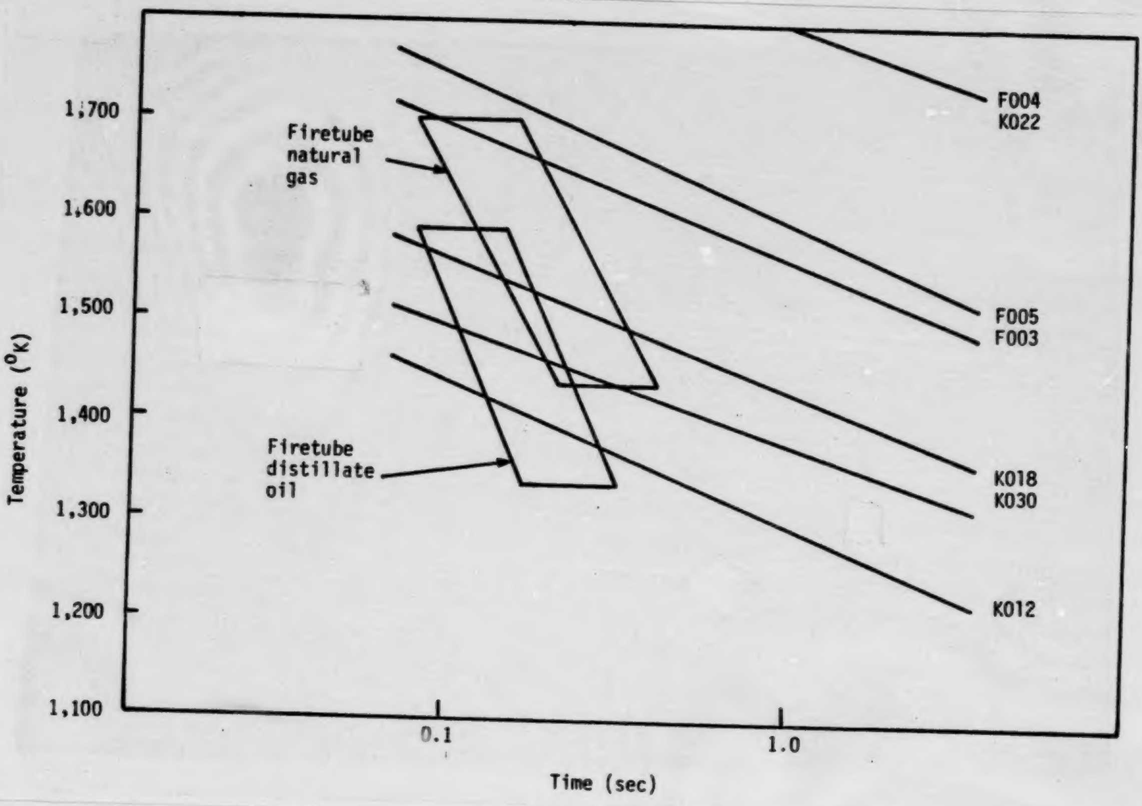

Figure 27. Stream destructibility predictions for firetube boilers.

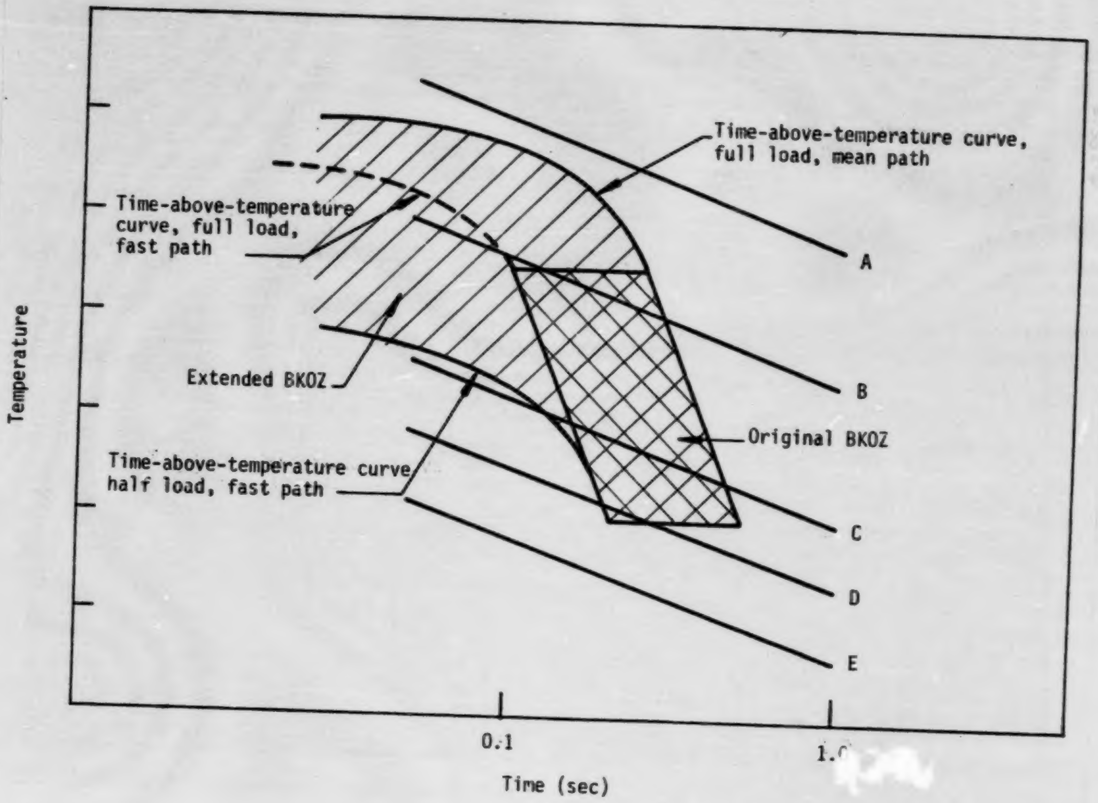

Figure 28. Example of an extended BKOZ.

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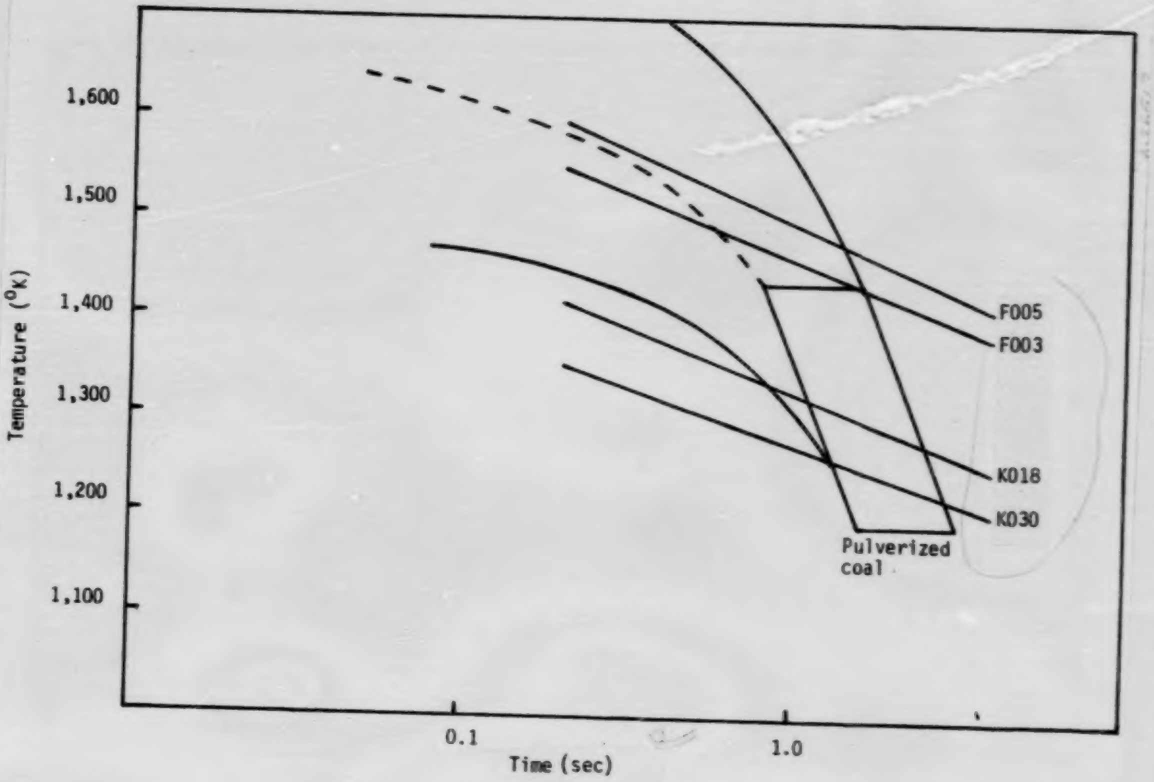

Figure 29. Extended BKOZ for the pulverized-coal boiler.

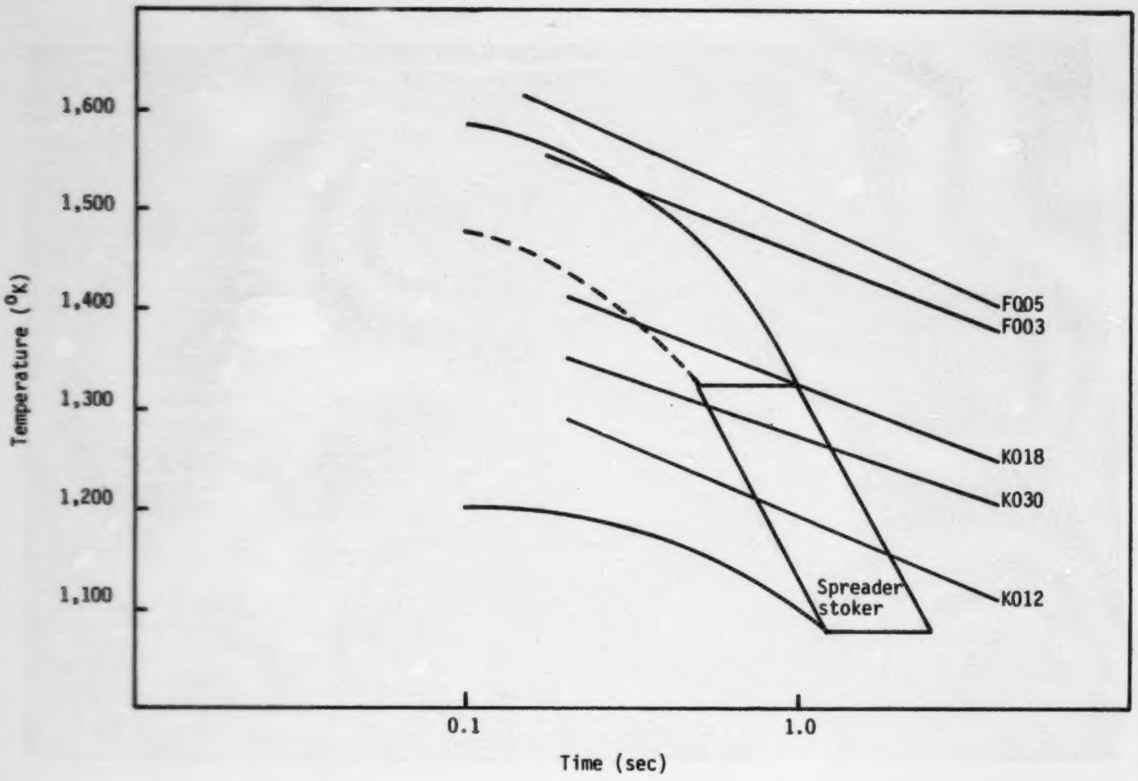

Figure 30. Extended BKOZ for the spreader-stoker boiler.

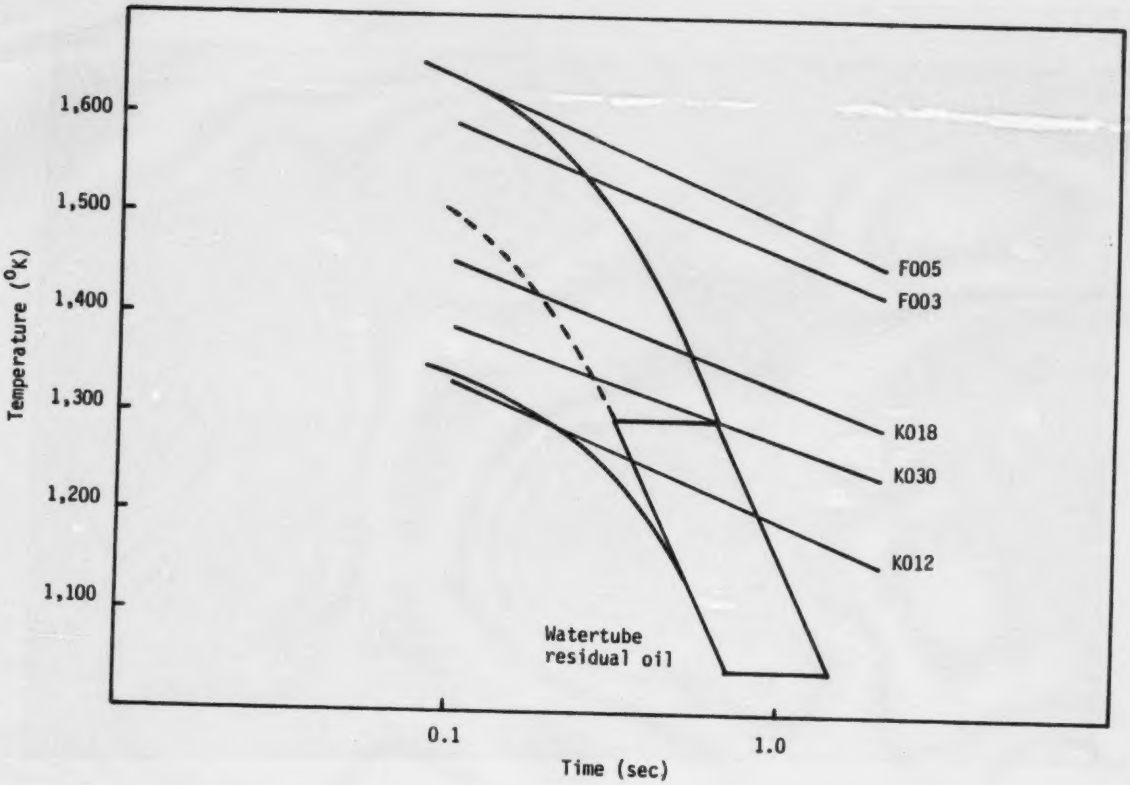

Figure 31. Extended BKOZ for the residual oil-fired watertube boiler.

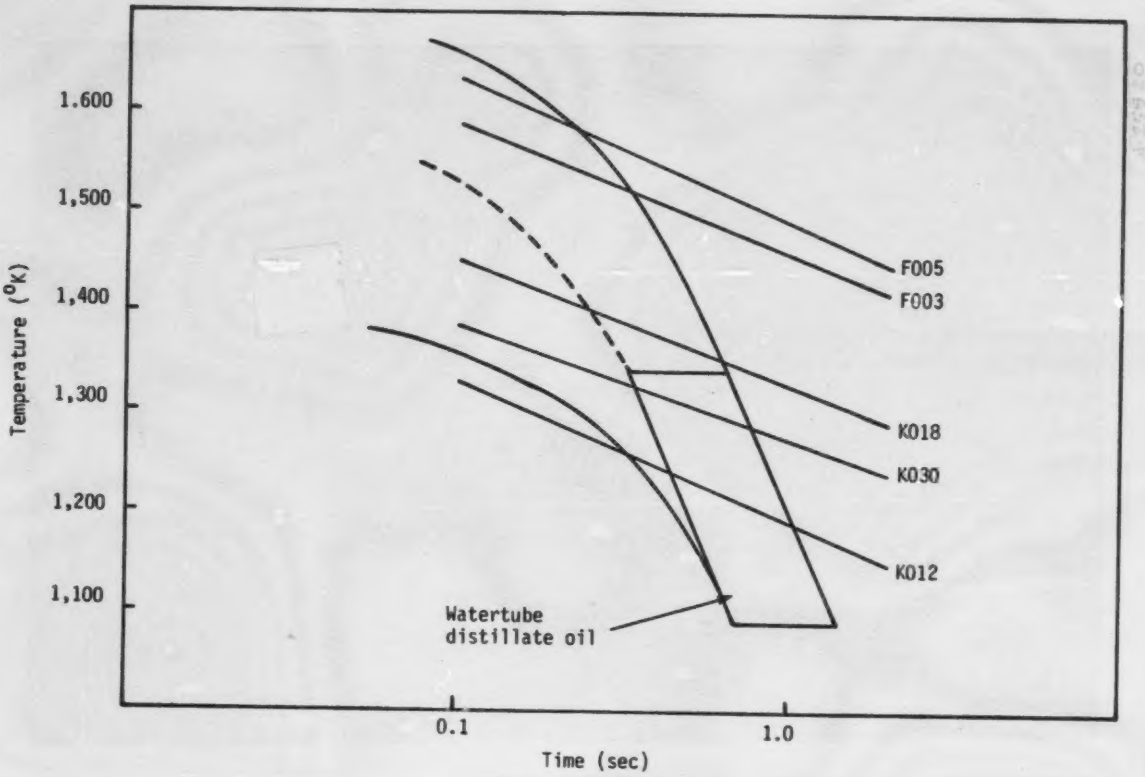

Figure 32. Extended BKOZ for the distillate-oil-fired watertube boiler.

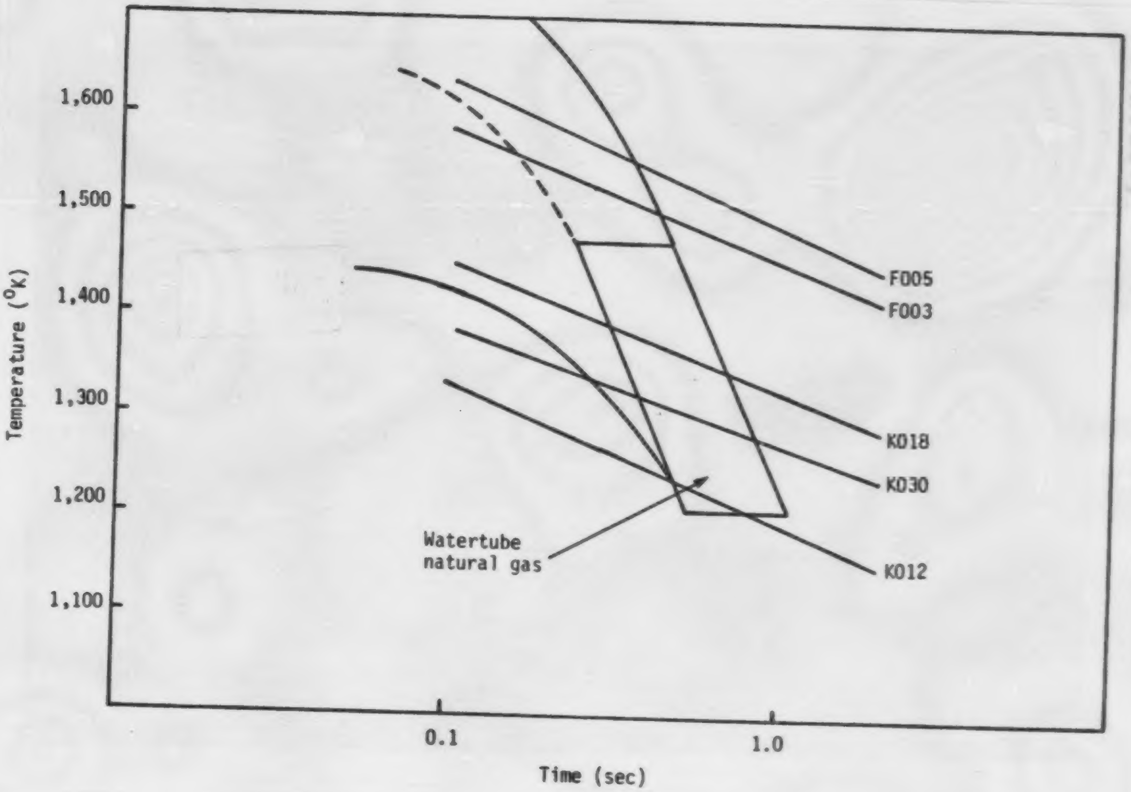

Figure 33. Extended BKOZ for the natural-gas-fired watertube boiler.

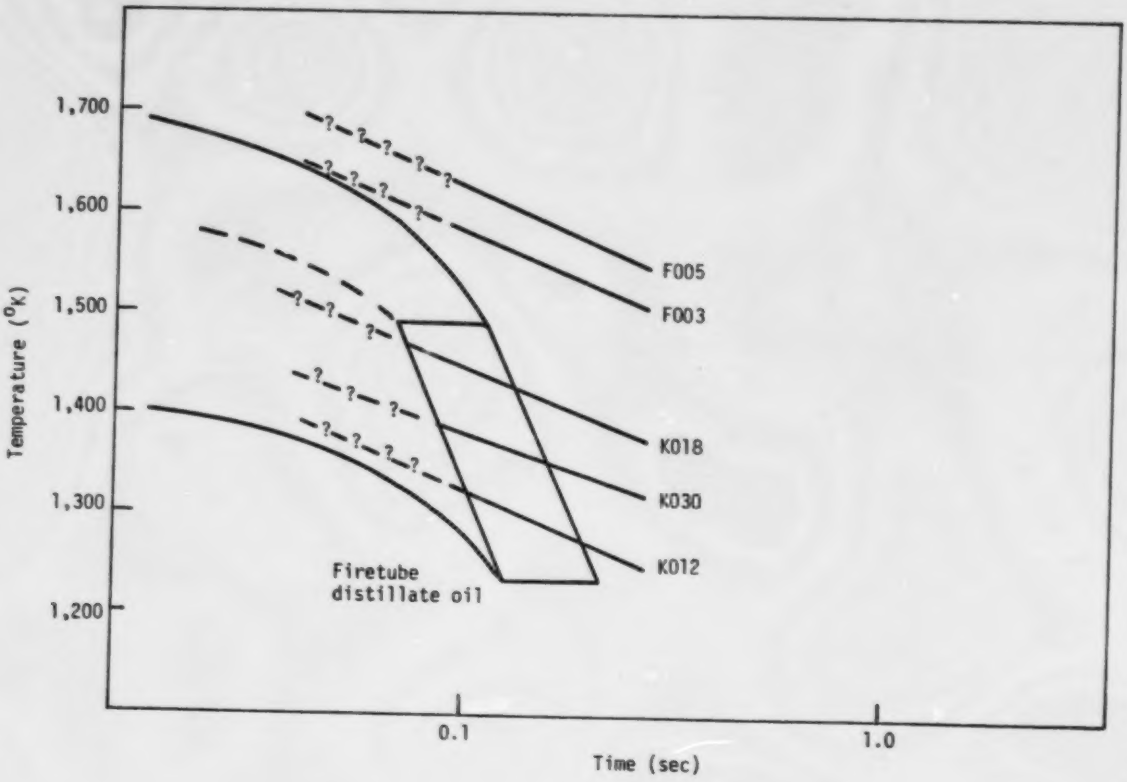

Figure 34. Extended BKOZ for the distillate-oil-fired firetube boiler.

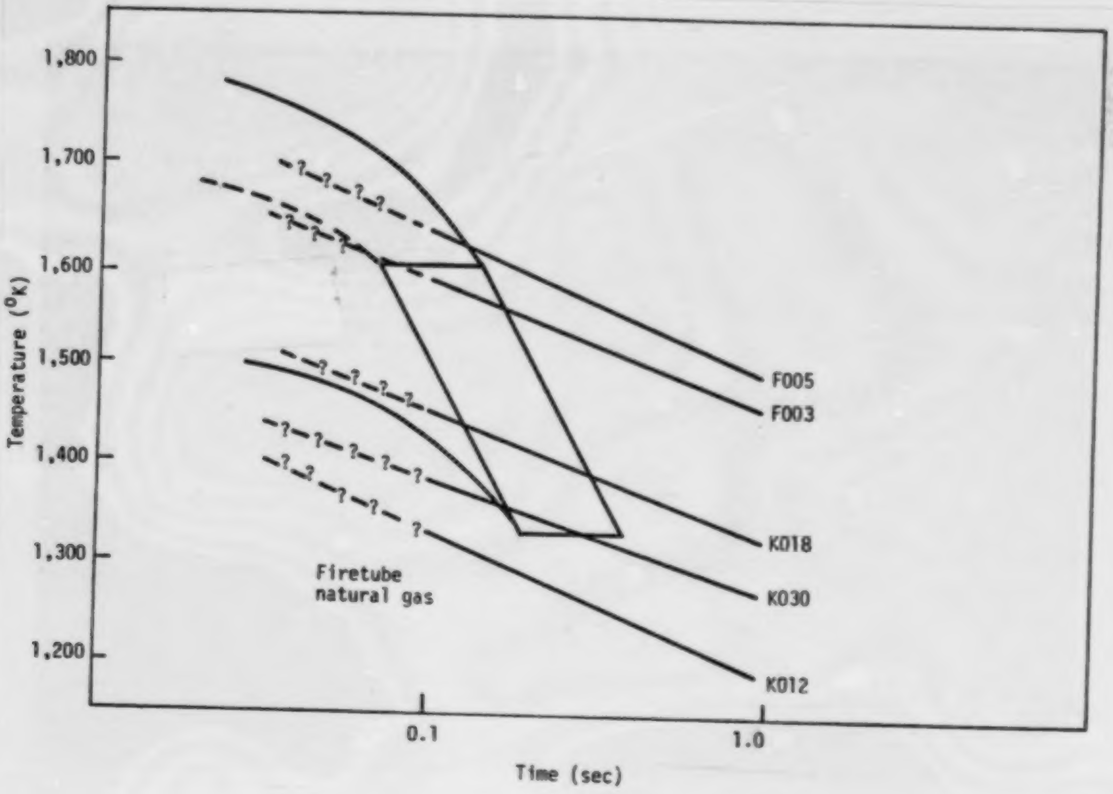

Figure 35. Extended BKOZ for the natural-gas-fired firetube boiler.

TABLE 35. APPLICABILITY OF VARIOUS BOILERS TO THE GAS PHASE PYROLYSIS OF GIVEN STREAMS -- EXTENDED CONSERVATIVE ESTIMATE (USING TIME ABOVE TEMPERATURE)

	Hazardous waste number						
Boiler	F003	F004	F005	K012	K018	K022	K030
G: 58.6 MW (200 million Btu/hr) Pulverized coal-fired watertube							
Full load	A	N	X	A	A	N	A
Half load	N	N	N	A	A	N	A
F: 44 MW (150 million Btu/hr) Spreader stoker-fired watertube							
Full load	X	N	N	A	A	N	A
Half load	N	N	N	X	N	N	N
E: 44 MW (150 million Btu/hr) Residential oil-fired packaged watertube							
Full load	X	N	N	A	A	N	A
Half load	N	N	N	A	N	N	X
D: 44 MW (150 million Btu/hr) Distillate oil-fired packaged watertube							
Full load	X	N	X	A	A	N	A
Half load	N	N	N	A	X	N	X
C: 44 MW (150 million Btu/hr) Natural gas-fired packaged watertube							
Full load	A	N	X	A	A	N	A
Half load	N	N	N	A	X	N	A

(continued)

TABLE 35. (continued)

Boiler	Hazardous waste number						
	F003	F004	F005	K012	K018	K022	K030
B: 4.4 MW (15 million Btu/hr)							
Distillate oil-	A	N	X	A	A	N	A
fired packaged	N	N	N	A	A	N	A
firetube							
Full load	N	N	N	A(?)	A(?)	N	A(?)
Half load	N	N	N	X(?)	N	N	X(?)
A: 4.4 MW (15 million Btu/hr) Natural gas-fired packaged firetube							
Full load	A(?)	N	X(?)	A	A	N	A
Half load	N	N	N	A	X	N	A

A -- Applicable
X -- Marginally applicable (composite compound line passes below mean path, but above fast path)
N -- Not applicable (composite compound line is above mean path)

SECTION 8

SECONDARY IMPACTS OF HAZARDOUS WASTE COFIRING

Incremental emissions arising from the cofiring of hazardous wastes may occur in all three emission categories: solids, liquids, and gases. Solids will arise primarily from contaminated containers, bottom and flyash, slag, and treatment sludges. Liquids (contaminated water) will be associated with plant runoff and scrubber effluents. Gas emissions will occur in the flue gas (along with uncontrolled flyash) and as fugitive emissions around handling areas.

Modifying and operating an industrial boiler for hazardous waste cofiring may thus cause numerous impacts on facility design and operation. This section reviews the two major impacts, source emissions and source operation.

8.1 FLUE GAS AND FUGITIVE EMISSIONS

The bulk of emissions will occur in the flue gas. These will fall into the classification of criteria pollutants (CO, SO_x, NO_x, particulates) and products of incomplete hazardous waste combustion (PIC's). The PIC's, in turn, may be gaseous, condensed liquids, or condensed solids, depending on exit gas temperatures.

Fugitive emissions will occur during the handling of wastes with a high content of volatile components. Under good operating procedures, these concentrations should be negligible.

8.1.1 Flue Gas Emissions

The majority of the organic hazardous wastes suitable for thermal destruction may be classified on the basis of their elemental composition or potential products of complete combustion. Criteria pollutant emissions (CO, NO_x, and SO_x) as well as other emissions such as HCl, HCN, and P_2O_5, will be dependent on this elemental composition. Table 36 lists hazardous wastes elemental compositions, examples of origin of each waste class and the combustion products from the assumed complete oxidation-decomposition of the waste.

Actual wastes will contain particulate material such as dirt and scale, as well as trace elements from corrosion, catalysts, and feedstock sources. The inorganic content of the hazardous wastes will be oxidized, and depending

TABLE 36. ELEMENTAL COMPOSITION AND PRODUCTS OF COMPLETE COMBUSTION

Waste class	Chemical elements	Examples (waste origin)	Combustion products after total decomposition
1	Carbon and hydrogen	Tars from production of styrene	CO_2, H_2O, N_2, NO_x
	Carbon, hydrogen and oxygen	Off-specification phenol	CO_2, H_2O, N_2, NO_x
2	Carbon, hydrogen and nitrogen	Solid residue from manufacture of aromatic amines	CO_2, H_2O, N_2, NO_x
	Carbon, hydrogen, nitrogen and oxygen	TDI manufacture reactor tar bottoms	CO_2, H_2O, N_2, NO_x
3	Carbon, hydrogen and chlorine	Vinyl chloride monomer manufacturing wastes	CO_2, H_2O, N_2, HCl(g), NO_x
	Carbon, hydrogen, chlorine and oxygen	Phenolic tar from 2,4-D manufacture	CO_2, H_2O, N_2, HCl(g), NO_x
4	Carbon, hydrogen, chlorine and nitrogen	Nitrochlorobenzene manufacturing wastes	CO_2, H_2O, N_2, HCl(g), NO_x
	Carbon, hydrogen and sulfur	Petroleum refining sour waste	CO_2, H_2O, N_2, NO_x, SO_x
	Carbon, hydrogen and fluorine	Fluorinated herbicide wastes	CO_2, H_2O, N_2, HF(g), NO_x
	Carbon, hydrogen and bromine	Ethylene bromide manufacturing waste	CO_2, H_2O, N_2, NO_x, HBr
	Carbon, hydrogen and phosphorus	Malathion	CO_2, H_2O, N_2, NO_x, P_2O_5
	Carbon, hydrogen and silicon	Tetraethyl orthosilicate wastes	CO_2, H_2O, N_2, NO_x, Particulate (silica)
	Carbon, hydrogen and sodium	Refinery spent caustic	CO_2, H_2O, N_2, NO_x, Particulate (Na_2O)

upon the volatility of the wastes, the combustion products will contain gaseous or particulate inorganic oxides.

The thermal decomposition properties of all wastes within one class will not be the same. Within each class, solid hazardous wastes may degrade differently from liquids, and liquids containing a high percentage of combustible hydrocarbons will decompose differently from slurries containing a high percentage of water but which are low in combustible hydrocarbons. The incentive for examining the method of disposal of hazardous wastes by thermal destruction is to minimize the objectionable environmental impacts with alternate disposal methods. Foremost among the concerns in the thermal destruction method is the possibility of PIC formation in the boiler.

Studies of PIC formation are almost exclusively limited to the formation of polycyclic organic matter POM's and the combustion products of chlorinated aromatics. The emphasis on chlorinated aromatics arises from the deep concern for chlorinated dibenzofurans and chlorinated dibenzo-p-dioxins. Although it has been conclusively shown that such PIC's do form under thermal destruction conditions for several classes of compounds, there is still much debate over the survival of such compounds as they pass through a combustion zone. From the limited test data available (almost exclusively on incinerators designed for complete combustion) these compounds survive in the flue gas or on flyash in only the smallest measureable concentrations, if at all. Conversely, there are positive indications of PIC's associated with polychlorinated aromatics occurring in bottom ash. For other classes of organic compounds, there is essentially no available quantitative data on PIC formation.

Assuming that the chemical components of combustible hazardous wastes are carbon, hydrogen, oxygen, nitrogen, chlorine, sulfur, etc., oxidation of these elements will produce incremental emissions of CO_2, H_2O, N_2, NO_x, SO_x, HCl and other gases. The relative contribution of incremental criteria pollutant emissions from thermal destruction of hazardous wastes in the boiler is dependent upon the ratio of hazardous wastes to primary fuel that is being utilized in the industrial boiler. The impacts of these emissions to the environment will again depend upon the efficiency of the pollution control device that will be used for the boiler.

Warnings of accidental release of hazardous wastes to the atmosphere can be provided by online continuous analyzer and monitoring instrumentation. Real-time determination of PIC's and hazardous waste components is not feasible. Typical analyzers that may be employed are:

CO_2 and CO -- Nondispersive infrared
O_2 -- Paramagnetic
HC -- Flame ionization detector
NO/NO_x -- Chemiluminescence

Set point limits of these analyzer/monitors should be linked to the boiler instrumentation panel for audio and visual signals. Carbon dioxide (CO_2) and oxygen (O_2) readings provide information on excess air in the combustion products. Carbon monoxide (CO) and hydrocarbon (HC) data indicate to what extent the combustibles have been oxidized. Hydrocarbon and carbon monoxide concentration data normally are used to determine if destruction of the wastes has been completed.

The major emissions from fossil fuel burning boilers are particulates, sulfur oxides (SO_x), nitrogen oxides (NO_x), hydrocarbons, and carbon monoxide (CO). Polycyclic organic matter (POM's) are among the hydrocarbon species that may be discharged into the atmosphere from the boiler. Many hazardous wastes contain high nitrogen levels. Such nitrogenous wastes when oxidized in the boiler's combustion chamber may produce increased quantities of nitrogen oxides, though 100 percent conversion of waste nitrogen to NO_x would not be expected as this is not the case for fuel bound nitrogen conversion in coal and oil firing. In addition to gaseous pollutant emissions, trace elements are discharged along with particulate matters to the atmosphere. Contaminated scrubber water and sludges also may be problem pollutant sources that will need to be considered in hazardous waste destruction facilities.

In the following case studies, the incremental emissions due to hazardous waste incineration will be examined. Note that there is no information on PIC's.

Case Study No. 1 -- Ethylene Manufacturing Waste (Ref. 47)

The waste obtained was a clear, light-brown solution with no apparent sediment or particulate at room temperature. It had a specific gravity of about 0.9 and a heating value of slightly more than 41.8 MJ/kg (18,000 Btu/lb) The chemical composition was approximately 89 percent carbon and 9 percent hydrogen. Halogens (as chlorine) were about 0.004 percent. Sulfur and nitrogen contents were 1.3 and 0.13 percent, respectively. A viscosity of 1.28 centistokes (at 22°C) allowed this material to be transferred and injected into an incinerator without preheating or other conditioning. Organic components of the waste, summarized in Table 37, were primarily unsaturated cyclic and aromatic compounds. No organic sulfur compound could be identified. Thus, the 1.3 percent sulfur found by elemental analysis was most likely present in an inorganic form. The total inorganic (ash) content of the ethylene waste was less than 0.01 percent. Trace elemental analysis showed no metals present at greater than 1 ppm levels.

The gas composition for the combustion of fuel oil and for ethylene wastes are nearly identical. Even with high excess air, the incinerator produced CO and HC (see Table 38). This indicates that total oxidation of hazardous wastes will not be easy. SO_2 levels for the ethylene waste were high due to the sulfur content in the waste. NO_x levels from the combustion of ethylene waste were comparable to fuel oil combustion. The operation of the incinerator is summarized in Table 39.

TABLE 37. COMPOSITION OF ETHYLENE MANUFACTURING WASTE SAMPLE (REF. 47)

Compound	Approximate concentration (wt percent)
Cyclopentadiene	<0.1
1, 3, 5-hexatriene	<0.1
Methylcyclopentadiene	<0.1
Benzene	30
Cyclohexadiene	20
Toluene	20
Xylene	3
Styrene	20
Methyl styrene	0.8
Indene	5.0
Methylindene and divinyl benzene	1
Naphthalene	3
Ethyl naphthalene	0.2

TABLE 38. TOTAL GAS COMPOSITION IN THE COMBUSTION ZONE BY VOLUME (REF. 47)

Run no. and fuel description	O_2 (%)	CO_2 (%)	N_2 (%)	H_2O (%)	HCl (ppm)	Cl_2 (ppm)	CO (ppm)	NO_x (ppm)	HC (ppm)	SO_2 (ppm)
Fuel oil background										
I	6.3	9.8	73.0	10.9	--	--	12	170	10	15-20
Ethylene waste										
II	7.2	10.3	74.0	8.5	--	--	17	200	5-10	100-200
III	9.4	9.3	73.4	7.9	--	--	17	150	5-15	100-200
IV	4.9	11.5	74.2	9.4	--	--	22	520	5	100-200
C-5,6 + fuel oil										
V	8.1	8.4	69.6	12.7	1.15	0.05	20	145	10-25	5
VI	5.6	9.7	68.8	14.2	1.64	15	17	140	35-65	6
VII	5.5	9.5	67.9	14.7	2.35	56	17	120	30-35	5

TABLE 39. INCINERATION RESULTS SUMMARY (REF. 47)

	Ethylene waste	C-5,6 waste
Combustion temperature (°C)	1,349-1,752	1,348-1,378
Residence time (s)	0.14-0.19	0.17-0.18
Feed rate (kg/min)	1.4-2.0	2.0-2.9[a]
Particulate (mg/m^3)	20-25	36-113[b]
Trace metals (mg/m^3)	0.001-0.003 Pb	0.003-0.006 Pb 0.034-0.065 Mn
Quality of combustion gas		
Total organics (mg/m^3)	13-22	21-27
Waste content (mg/m^3)	Not detected (<0.02)	Not detected (<0.02)
Trace metals (mg/m^3)	0.002-0.003 Pb	0.55-1.40 Pb 0.077-0.19 Mn 0.090-0.030 Co
Quality of scrubber water		
Total organics (mg/liter)	Not significant[c]	Not significant[c]
Trace metals (mg/liter)	0.002 Pb	0.21-0.54 Pb
Quality of solid residue (clinker)		
Waste content (mg/g)	1.8-2.4	Not detected (<0.026)
Destruction efficiency		
Total organics (percent)	99.95-99.96	99.94-99.95
Waste constituents (percent)	>99.999	>99.999

[a] Mixture of C-5,6 and No. 2 oil; feed rate of C-5,6 alone is 0.66-1.5 kg/min.

[b] 85-90 percent of stack particulate content was calculated (based upon sodium analysis) to be NaCl produced by the reaction of the caustic scrubber solution with HCl and CO_2.

[c] Levels not significantly higher than background water samples.

Case Study No. 2 -- Hexachlorocyclopentadiene Manufacturing Waste (Ref. 47)

This highly chlorinated waste is produced at a rate of 4.5 Gg annually. It would not sustain combustion without auxiliary fuel; its heating value was only 5.6 MJ/kg (2,400 Btu/lb). The C-5,6 waste was a dark brown liquid with suspended, waxlike particulate matter. Specific gravity was in excess of 1.7, while its viscosity was 11.3 centistokes (at 22°C). The waste was miscible in no. 2 fuel oil which facilitated injection and combustion in the liquid incinerator. The chemical composition of a sample of the C-5,6 waste was approximately 21 percent carbon, 0.67 percent hydrogen, 0.37 percent nitrogen, 0.016 percent sulfur, and 77 percent total halogens (as chlorine). Hexachlorocyclopentadiene (C_5Cl_6) and octachlorocyclopentene (C_5Cl_8) were the major organic waste components found in two separate samples of the C-5,6 waste, as shown in Table 40.

The total inorganic (ash) content of a sample of the waste was less than 0.04 percent. Elemental inorganics found were primarily innocuous metals, such as Fe, Si, Al, Na, and Ca. Lower and trace (ppb) levels were found for numerous elements.

The NO_x levels from C-5,6 wastes were lower than for fuel oil combustion suggesting that thermal NO_x production in C-5,6 waste is lower than fuel oil (see Table 38). The reason may be due to high water content of the waste and consequent lower combustion zone temperatures.

Case Study No. 3 -- Fluidized Bed Incineration of Phenol and Methyl Methacrylate Wastes (Ref. 48)

In Tables 41 and 42, the organic composition and trace metal contents of the phenol waste are noted. Similarly, the organic composition and trace metal contents of the methyl methacrylate wastes are given in Tables 43 and 44 Table 45 summarizes the incineration parameters for the destruction of the above two chemical wastes. Table 46 tabulates the composition of the flue gases produced in the incineration of the phenol and methyl methacrylate wastes. The trace metal concentrations in the stack gases produced in the above incineration process are shown in Table 47.

Analyzing the results of test numbers I and III against test no. II (Table 46), it is noted that NO_x levels in phenol combustion process are four to five times higher than for the fuel oil burning (test no. II).

The presence of CO and HC in the flue gas indicates incomplete combustion of the hydrocarbon elements of the waste. Incomplete combustion may have occurred due to inefficient mixing with air and insufficient residence time at proper temperatures. Incomplete combustion of a hydrocarbon fuel also suggests insufficient heat release from the oxidation process. The presence of CO and HC in the flue gas is not necessarily an indication that inadequate waste destruction has occurred. CO and HC may have originated from carrier chemicals or may have originated in oxidation reactions.

TABLE 40. COMPOSITION OF HEXACHLOROCYCLOPENTADIENE WASTE (REF. 47)

Compound	Approximate concentration (wt percent)
C_5Cl_6 (hexachlorocyclopentadiene)	50-65
C_5Cl_7 (heptachlorocyclopentene)	3-5
C_5Cl_8 (octachlorocyclopentene)	30-45
Other minor constituents	1-2

TABLE 41. ORGANIC COMPOSITION OF PHENOL WASTE REPRESENTATIVE SAMPLE (REF. 48)

Compound	Estimated level in the waste sample (wt percent)[a]
Ethanol	0.06
Acetone	0.07
2-Butanone (MEK)	0.05
Butanol	<0.01
2-Ethoxyethanol	0.07
Toluene	0.3
Xylene (two isomers)	0.6
Isopropyl benzene	0.8
Phenol	3.7
o-Cresol	0.9
m-Cresol	1.9

[a] Sample contained 86 percent water and approximately 5.5 percent nonignitable solids.

TABLE 42. TRACE METALS IN THE PHENOL WASTE (REF. 48)

Element	Approximate concentration in waste (ppm)	Calculated theoretical concentration in combustion gas (mg/m^3)
Ca	310	26
Si	240	20
Al	86	7.3
K	75	6.4
Mg	40	3.4
P	33	2.8
Pt	16	1.4
Ti	15	1.3
Sn	6	0.5
Zn	6	0.5
V[a]	5	0.4
Cr[a]	4	0.3
Cu	4	0.3
Mo	4	0.3
Zr	4	0.3
Mn	3	0.3
Pb[a]	3	0.3
B	1	0.1
Ba[a]	1	0.1
Ce	1	0.1
Nb	1	0.1
Ni	1	0.1
La	0.6	0.05
Cd[a]	0.5	0.04
Sr	0.5	0.04
Li	0.3	0.03
Nd	0.2	0.02
Ag	0.1	0.01
Hg[a,b]	0.1	0.01
Rb	0.1	0.01
Y	0.1	0.01
Sb[a]	0.08	0.007
Se[a]	0.06	0.005
As[a]	0.03	0.003
Be[a]	0.01	0.001
Co[a]	0.01	0.001

[a] Potentially toxic metals -- ACGIH TLV of <1 mg/m^3 for an 8-hour exposure. (Ref. 48)

[b] Determined by atomic fluorescence.

TABLE 43. ORGANIC COMPOSITION OF METHYL METHACRYLATE WASTE REPRESENTATIVE SAMPLE (REF. 48)

Compound	Estimated levels (wt percent)[a]
Methanol	4.9
Acetone	0.7
Methylene chloride	0.7
2-Butanone	1.1
Methyl propanoate	0.4
Methyl methacrylate	33.9
2-Ethoxy ethanol	0.4
Toluene	1.1
Xylene	0.9
2-Ethoxy ethyl acetate	0.4
Phenol	12.6
Cresols	3.4

[a] Sample contains 38 percent water and approximately 1.7 percent nonignitable solids.

TABLE 44. TRACE METALS IN THE MMA WASTE (REF. 48)

Element	Approximate concentration in waste (ppm)	Calculated theoretical concentration in combustion gas (mg/m^3)
Al	160-315	9-18
Ca	160-315	9-18
Pb[a]	160-315	9-18
Si	110	6.4
Mg	75	4.4
P	57	3.3
Cr[a]	38	2.2
Fe	38	2.2
Ba	35	2.0
Zn	26	1.5
Cd[a]	21	1.2
Cu	19	1.1
Mn	10	0.6
Pt	4	0.2
Sn	4	0.2
Bi	2	0.1
K	2	0.1
Mo	2	0.1
Ni	2	0.1
Sb[a]	2	0.1
Sr	2	0.1
Ag	0.4	0.02
Co[a]	0.4	0.02
Zr	0.4	0.02
B	0.2	0.01
Rb	0.2	0.01
V[a]	0.2	0.01
Nb	0.1	0.006
W	0.1	0.006
As[a,b]	0.04	0.002
Hg[a,b]	0.03	0.002
Be[a]	0.006	0.0003
Se[a]	0.004	0.0002

[a] Potentially toxic metals -- ACGIH TLV of <1 mg/m^3 for an 8-hour exposure. (Ref. 48)

[b] Determined by atomic fluorescence.

TABLE 45. INCINERATOR SYSTEM PARAMETERS DATA SUMMARY (REF. 48)

Test no.	I	II	III	IV	V
Waste tested	Phenols	--[a]	Phenols	Methyl metha-crylate	Methyl metha-crylate
Waste/auxiliary fuel ratio	3.0:1[b]	--	2.3:1	2.0:1	2.6:1
Flowrates					
Waste (l/min)	49.9	--	33.6	29.5	36.4
Aux. fuel (l/min)	16.4	12.1	14.8	15.0	14.0
Fluidizing air (m^3/min)	350	435	425	425	425
Overbed air (m^3/min)	72	105	105	105	105
Scrubber quench water (l/min)	2.3	2.3	2.3	2.3	2.3
Scrubber seal water (l/min)	1.6	1.6	1.6	1.6	1.6
Temperatures					
Reactor bed TE-1 (°C)	734	782	760	774	791
Reactor bed TE-2 (°C)	757	779	763	777	791
Reactor bed TE-3 (°C)	721	766	749	771	782
Reactor bed controller (°C)	735	779	754	771	788
Reactor freeboard (°C)	899	793	813	824	843
Reactor duct north end (°C)	888	768	796	796	841
Scrubber inlet (°C)	85	76	80	80	82
Scrubber outlet (°C)	92	82	85	85	91
Pressures					
Waste feed pump (kPa)	270	--	190	140	190
Windbox (cm H_2O)	152	157	168	168	163
Bed differential (cm H_2O)	81	79	86	81	81
Freeboard (cm H_2O)	8.9	10.7	17.8	15.7	14.7
Exhaust oxygen (percent)	9.6[c]	14.8	17.7	14.5	14.1
Calculated residence time (s)	14	12	12	12	12

[a] Background test with auxiliary fuel (No. 2 oil) only.

[b] Volumetric flow ratio -- liters per minute waste/liters per minute auxiliary fuel.

[c] Oxygen content of exhaust gases in stack as measured by site personnel.

TABLE 46. GAS COMPOSITION DATA SUMMARY (REF. 48)

Test No.	O_2 (percent)	CO_2 (percent)	CO (ppm)	NO_x (ppm)	N_2 (percent)	HC (ppm)[a]	EA[b] (percent)
I	10.7	9.4	6-7	56	79.9	5-20	101
II	15.4	5.9	5	10	78.7	10-50	278
III	12.6	7.6	8-26	41-51	79.8	0-33	146
IV	13.4	7.4	8-10	--[c]	79.2	0-40	175
V	11.6	8.0	10-20	--[c]	80.4	0-10	119

[a] As methane.

[b] Excess air.

[c] Instrument was down due to a broken power supply.

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TABLE 47. SURVEY FOR TRACE METALS IN THE STACK FILTER DIGESTS BY ICAP (REF. 48)

Element ppm	Test II (background) (ppm)	Test III (phenol) (ppm)	Test V (MMA) (ppm)
Al	≤0.55[a]	≤0.72	≤0.83
Ba	≤0.44	≤0.90	≤0.44
B	≤0.83	≤1.5	≤0.38
Ca	≤0.55	≤1.01	≤1.6
Cd	0.007	0.016	0.15
Cr	0.036	0.061	0.13
Cu	0.035	0.47	0.38
Fe	0.15	4.5	0.56
Pb	0.082	0.40	2.3
Mg	≤0.36	≤0.31	≤0.53
Mn	≤0.004	≤0.015	≤0.013
Ni	0.004	0.012	ND (0.0002)
P	0.075	0.31	0.68
K	ND (0.012)	3.1	2.4
Si	≤0.28	≤0.09	≤0.07
Ag	≤0.004	≤0.001	≤0.013
Na	2.7	89	23
Sr	≤0.015	≤0.017	≤0.018
Ti	≤0.082	≤0.048	≤0.088
V	0.0005	0.0015	0.0008
Zn	≤0.15	≤0.28	≤0.22

[a] "≤", a less than or equal to sign indicates those elements which were detected but not significantly above background levels.

Note
ICAP = Ion coupled argon plasma spectroscopy.

Examining the data of Tables 44 and 47, it is observed that the scrubber was effective in reducing the trace elements from both the waste's effluent gas streams. It is important to note the separated trace elements will find their way to the scrubber water and sludge. Oil and gas burning industrial boilers seldom use any pollution control device; when such boilers are utilized to destroy hazardous wastes for which a scrubber will be required, the presence of trace elements in scrubber water and sludges may be considered as incremental emissions of a hazardous waste thermal destruction process. Sludges that contain high concentrations of toxic trace elements could only be disposed safely in specially designed landfills. Similarly, scrubber waters that contain high concentrations of trace elements and polycyclic organic matter (POM) could not be discharged to city sewers without proper treatment.

Case Study No. 4 -- Emissions from Coal- and Oil-Fired Controlled Industrial Boilers (Ref. 49)

Tables 48 through 52 summarize results of criteria pollutants and trace element emissions from coal-and oil-fired industrial boilers from a comprehensive assessment of emissions (pre and postscrubber) from these units. (Ref. 49)

Comparing the criteria pollutant emissions from the coal-and oil-fired boilers (Tables 48 and 49) with emissions from the incineration of hazardous wastes (case studies 1 and 2), it is noted that all categories of criteria pollutant emissions for coal and oil-fired boilers are many times higher.

When hazardous waste is used as supplemental fuel, conventional fossil fuels are displaced by the equivalent heat input of the hazardous wastes. The net emissions of criteria pollutants from cofiring hazardous wastes and a fossil fuel, may not increase above the emissions level of a simple fossil fuel (coal/oil) fired boiler. For many hazardous wastes with heating values comparable to fossil fuels (coal/oil), the overall net emissions of criteria pollutants may decrease. For many of the aqueous mixtures of hazardous wastes with low heating values, the amount of hazardous wastes for an equivalent heat input of the displaced fossil fuel will be high, but the net emission may still be lower than a single fossil fuel-fired boiler.

Tables 50 and 51 list trace element emissions from coal-and oil-fired boilers. These emissions are many times higher than for typical hazardous wastes. Therefore, by cofiring hazardous wastes with coal or oil as the primary fuel, the level of trace element emissions may not increase above those levels generated from a simple fossil-fuel-fired boiler. It is noted that trace element mass emissions from coal-fired boilers are higher than from oil-fired boilers by a factor of about 80.

Table 52 summarizes the annual emissions resulting from firing coal and oil in industrial boilers. The data show that NO_x, CO, and sulfate emissions from coal-fired boilers exceed those from oil-fuel-fired boilers by more than a factor of 3. Since the emissions of these compounds from hazardous wastes firing are lower than from firing either coal or oil, the combined net

TABLE 48. SUMMARY OF CRITERIA POLLUTANT EMISSIONS -- COAL FIRING (REF. 49)

Test no.	ng/J (lb/million Btu)							
	NO_x (as NO_2)	CO	SO_2	HC (as CH_4)	C_1 to C_{16} Organics	C_7 to C_{16} Organics	Organics higher than C_{16}	Total particulates
200 Inlet	417 (0.97)	20.7 (0.05)	1,009 (2.35)	3.79 (0.01)	<5.49 (<0.01)	0.34 (0.00)	2.28 (0.01)	2,361 (5.49)
200 Outlet	367 (0.85)	18.5 (0.04)	25.4 (0.06)	4.22 (0.01)	<5.49 (<0.01)	0.27 (0.00)	0.33 (0.00)	14.3 (0.03)
201-1 Inlet	491 (1.14)	16.5 (0.04)	1,284 (2.99)	4.35 (0.01)	<5.65 (<0.010)	--	--	3,122 (7.26)
201-1 Outlet	457 (1.06)	15.7 (0.04)	39.0 (0.09)	5.22 (0.01)	<5.65 (<0.01)	--	--	20.9 (0.05)
201-2 Inlet	455 (1.06)	17.7 (0.04)	1,295 (3.01)	0.88 (0.00)	<5.75 (<0.01)	--	--	--
201-2 Outlet	358 (8.33)	15.9 (0.04)	35.5 (0.08)	1.33 (0.00)	<5.75 (<0.01)	--	--	--
201-3 Inlet	330 (0.77)	16.2 (0.04)	1,028 (2.39)	10.9 (0.03)	<5.69 (<0.01)	--	--	--
201-3 Outlet	258 (0.60)	12.7 (0.03)	31.8 (0.07)	10.9 (0.03)	<5.69 (<0.01)	--	--	--
201-4 Inlet	409 (0.95)	8.56 (0.02)	942 (2.19)	8.95 (0.02)	<5.06 (<0.01)	--	--	3,370 (7.84)
201-4 Outlet	420 (0.98)	8.95 (0.02)	49.7 (0.12)	9.73 (0.02)	<5.06 (<0.01)	--	--	20.6 (0.05)
Average inlet	421 (0.98)	15.9 (0.04)	1,112 (2.59)	5.79 (0.01)	<5.53 (<0.01)	0.34 (0.00)	2.28 (0.01)	2,951 (6.86)
Average outlet	372 (0.87)	14.3 (0.03)	36.3 (0.08)	6.29 (0.01)	<5.53 (<0.01)	0.27 (0.00)	0.33 (0.00)	18.6 (0.04)

TABLE 49. SUMMARY OF CRITERIA POLLUTANT EMISSIONS -- OIL FIRING (REF. 49)

	ng/J (lb/million Btu)							
Test no.	NO_x	CO	SO_2	HC[b] (as CH_4)	C_1 to C_{16} Organics	C_7 to C_{16} Organics	Organics higher than C_{16}	Total particulates
200-1 Inlet	175 (0.41)	5.08 (0.01)	938 (2.18)	2.84 (0.01)	<4.63 (<0.01)	--	--	166 (0.39)
200-1 Outlet	166 (0.39)	4.70 (0.01)	32.1 (0.07)	3.20 (0.01)	<4.63 (<0.01)	--	--	20.2 (0.05)
202-2 Inlet	175 (0.41)	5.30 (0.01)	1,075 (2.50)	4.61 (0.01)	<4.79 (<0.01)	--	--	--
202-2 Outlet	165 (0.38)	5.03 (0.01)	29.2 (0.07)	5.01 (0.01)	<4.79 (<0.01)	--	--	--
203-3 Inlet	181 (0.42)	6.22 (0.01)	1,085 (2.52)	1.71 (0.00)	<4.73 (<0.01)	--	--	--
203-3 Outlet	177 (0.41)	5.92 (0.01)	26.7 (0.06)	1.98 (0.01)	<4.73 (<0.01)	--	--	--
203-4 Inlet	141 (0.33)	5.30 (0.01)	874 (2.03)	0.82 (0.00)	<4.14 (<0.01)	--	--	59.0 (0.14)
203-4 Outlet	138 (0.32)	5.60 (0.01)	19.2 (0.04)	0.76 (0.00)	<4.14 (<0.01)	--	--	15.0 (0.03)
203 Inlet[b]	--	--	--	--	--	0.17 (0.00)	2.61 (0.01)	--
203 Outlet[b]	--	--	--	--	--	0.02 (0.00)	0.43 (0.00)	--
Average inlet	168 (0.39)	5.47 (0.01)	993 (2.31)	2.49 (0.01)	<4.57 (<0.01)	0.17 (0.00)	2.61 (0.01)	113 (0.26)
Average outlet	161 (0.37)	5.31 (0.01)	26.8 (0.06)	2.74 (0.01)	<4.57 (<0.01)	0.02 (0.00)	0.43 (0.00)	17.6 (0.04)

[a] Emission factors were computed assuming an O_2 concentration of 5.5 percent, the average concentration for test 202.

[b] Total hydrocarbons as determined by FID.

TABLE 50. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING COAL FIRING -- TEST 201-1 (REF. 49)

	Emission factor (ng/J)		Emission rate (g/hr)			
Trace element	Scrubber inlet	Scrubber outlet	Scrubber inlet	Scrubber outlet	Efficiency (percent)	Enrichment factor
Be[a]	0.04	0.001	5	0.09	98	3.7
Hg[b]	0.08	0.037	0.50	0.23	55	84
Ca	32	0.015	3,300	1.6	99	0.09
Mg	8.2	0.0046	860	0.48	99	0.11
Sb	1.6	0.010	170	1.1	99	1.2
As	3.4	0.092	350	9.7	97	5.3
B[a]	0.1	0.01	10	1.2	88	2.1
Cd	0.20	0.00042	21	0.044	99	0.4
Cr	1.1	0.054	120	5.7	95	9.5
Co	1.6	0.0050	160	0.53	99	9.6
Cu	4.1	0.0084	430	0.88	99	0.4
Fe	190	1.0	20,000	110	99	0.99
Pb	3.7	0.0088	380	0.92	99	0.5
Mn	0.34	0.0063	35	0.68	98	3.4
Mo	4.3	0.026	450	1.2	99	0.5
Ni	0.60	0.026	61	2.8	95	8.6
V	1.3	0.024	140	2.5	98	3.6
Zn	0.99	0.020	100	2.1	98	3.9
Se	1.4	0.041	140	4.3	97	5.8
Sr	4.7	0.024	500	2.5	99	0.9
Al	210	1.1	22,000	110	99	1.0
Zr	0.69	0.0075	72	0.79	99	2.1
Total	470	2.6	50,000	270	99	

[a] Appropriate values as determined by SSMS. The other values, with the exception of mercury, were determined by ICPOES analysis.

[b] Mercury was determined by cold vapor analysis of SASS train samples taken during test 200.

TABLE 51. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING OIL FIRING -- TEST 202-4 (REF. 49)

	Emission factor (ng/J)		Emission rate (g/hr)			
Element	Scrubber inlet	Scrubber outlet	Scrubber inlet	Scrubber outlet	Removal efficiency Δ	Enrichment factor
Be[a]	<0.0003	0.00003	<0.04	0.04	Unknown	>11.9
Hg[b]	0.0006	0.0001	0.05	0.006	87	1.48
Ca	0.13	0.022	16	2.7	83	2.03
Mg	0.10	0.0094	12	1.1	91	1.15
Sb	0.02	0.0019	2.5	0.23	91	1.15
As	0.049	0.0094	5.9	1.1	81	2.37
B	0.17	0.012	21	1.5	93	0.87
Cd	0.091	0.021	11	2.5	77	2.80
Cr	0.055	0.0057	6.7	0.69	90	1.26
Co	0.033	0.0038	3.9	0.46	89	1.43
Cu	0.18	0.002	21	0.27	99	0.15
Fe	1.6	0.088	190	11	95	0.69
Pb	0.065	0.0041	7.9	0.50	94	0.77
Mn	0.010	0.0013	1.2	0.15	87	1.58
Mo	0.072	0.0079	8.7	0.95	89	1.35
Ni	0.36	0.063	43	7.7	83	2.16
V	0.88	0.26	110	31	71	3.61
Zn	0.20	0.02	24	2.5	90	1.27
Se	0.016	0.002	2.0	0.23	87	1.43
Sr	0.014	0.0003	1.7	0.038	98	0.28
Al	1.9	0.15	220	18	92	1.0
Zr	0.0049	0.0003	0.59	0.038	94	0.79
Total	6.0	0.78	710	96	87	

[a] Beryllium was determined by SSMS. The other elements, except mercury, were determined by ICPOES.

[b] Mercury was determined by cold vapor analysis of SASS train samples taken during test 203.

TABLE 52. ANNUAL EMISSIONS (REF. 49[a])

	Pollutant	Scrubber inlet, kg/year			Scrubber outlet, kg/year		
		Coal firing	Oil firing	Coal/oil	Coal firing	Oil firing	Coal/oil
Gaseous	NO_x (as NO_2)	500,810	164,230	3.05	442,520	157,390	2.81
	SO_2	1,127,300	906,202	1.24	36,800	24,453	1.51
	SO_3	6,184	7,249	0.85	4,157	5,183	0.80
	$SO_4^=$	67,214	20,894	3.22	8,110	8,303	0.98
	CO	16,119	4,991	3.23	14,497	4,845	2.99
	Organics (as CH_4)	5,870	2,272	2.58	6,377	2,500	2.55
	$C_1 - C_6$[b]	<5,606	<4,164	--	<5,606	<4,164	--
	$C_7 - C_{16}$	345	155	2.22	274	18	15.2
	C_{16}^+	2,311	2,381	0.97	335	392	0.85
	Total particulates	2,991,700	53,832	55.6	18,856	13,686	1.38
	$<1\mu$	--	--	--	11,691	11,359	1.03
	$1 - 3\mu$	--	--	--	5,657	1,642	3.45
	$3 - 10\mu$	--	--	--	1,320	634	1.93
	$>10\mu$	--	--	--	188	0[c]	--
				m^3 per year			
Liquid	Blowdown/wastewater	~76,000	~76,000	~1	~76,000	~76,000	~1
	Cooling water	~86,000	~86,000	~1	86,000	~86,000	~1
Solid	Bottom ash	~778,600	~7,600	~103	~778,600	~7,600	~103
	Flyash	1,800,000	~15,000	~120	~1,800,000	~15,000	~120
	Scrubber cake	0	0	--	8,054,100	3,011,000	2.67

[a] Assuming 100 percent load, 45 weeks per year (7,560 hr/year).
[b] These values represent the detection limit of the instrument used.
[c] These values represent oil-firing particulate with a minimum of coal ash contamination.

emissions from hazardous wastes cofiring may be equal to or less than from coal or oil firing.

The data on Tables 48 through 52 illustrate the removal efficiency of the scrubber for each of the criteria pollutants. It is interesting to note that the efficiency of the scrubber for coal particulate removal is over 99 percent, but for particulates from oil firing, the removal efficiency is only approximately 75 percent. The lower removal efficiency achieved during oil firing is due to the increased fraction of the particulates smaller than the 3 micron size range. The same characteristics of the scrubber are exhibited for trace elements from the flue gas (Tables 50 and 51) of coal-and oil-fired boilers.

Particle size distributions obtained during liquid hazardous wastes firing should be the same or smaller than the size of the oil-fired particulates. Increased emissions of smaller particulates may therefore be expected in the cofiring of hazardous wastes with fuel oil or coal. Under such circumstances, a two-stage particulate control system may be desirable.

8.1.2 Fugitive Emissions

Possible sources of fugitive emissions from a hazardous waste thermal destruction facility are summarized below:

1. Waste handling
    - Receiving site (transfer from truck trailers and railroad cars)
    - Transfer to storage tanks and to processing stations
2. Waste processing
    - Mixing or blending
    - Heating
    - Stirring
    - Shredding or crushing
    - Drying
3. Waste feeding to boiler
    - Leakage from pump seals and valves
    - Leakage from blower seals and dampers
    - Leakage from transport pipes, ducts and conveyors
    - Leakage from burner assembly, fittings and recirculation lines
4. Waste evaporation/emission
    - Fumes from spilled liquid waste collection pit
    - Fine particle emissions from waste handling, processing and feeding stations
    - Fumes from gas cooling/cleaning system

5. Waste burning flue gas system

   - Leakage from boiler and accessories
   - Leakage from pollution control equipment

6. Waste residues

   - Scrubber wash water
   - Scrubber sludges
   - Hopper ash from the particulate boiler
   - Boiler bottom ash
   - Recycle -- water treatment facility

Facility system design to decrease the occurrences of fugitive emissions would include:

- Prevention designs for leakages from ducts, pipes, mechanical handling equipment
- Safety feature designs for pumps, blowers and fans
- Safe collection and containment of spills and leaks from equipment system
- Safe disposal method for spills, vacuum cleaners or line catches
- Provision for containment room for a waste processing station
- Use of mechanical handling equipment in transport of wastes

Even with the best engineering designs, fugitive emissions may occur in the plant facility. The following steps may reduce the occurrences.

Good Operating and Maintenance

Adoption of good operating and maintenance practices are essential to ensure control of fugitives. These include:

- Regular cleanup schedules for the operating area
- Immediate cleanup of small spills
- Scheduled cleanup procedures to remove dust, spills and accumulation of hazardous wastes from outside surfaces of the machines, equipment, ducts, pipes and fittings, and other plant facility fixtures
- Mandatory use of appropriate protective clothing and adherence to the safety regulations in the work area
- Complete recordkeeping for any mishaps, spills and work stoppage due to dangerous work environment
- Periodic refresher training programs for maintaining healthy work environment and safe work practices
- Periodic health check up programs for the workers

Monitoring and Measurement of Fugitive Emissions

A methodology to monitor the fugitive emissions from the hazardous waste destruction facility should be identified. Some of the monitoring steps to be considered include:

- Routine source leak test programs
- Scheduled measurements of dust concentrations for the work area (high-volume sampler tests)
- Analysis of dust constituents and particle size distribution measurements
- Scheduled measurement programs to detect emissions of pollutant gases in the work area
- Continuous instrumentation monitoring of pollutants from high emission risk areas
- Regular checkups of pump and blower seals
- Periodic measurements of emissions from bag filter system
- Accurate records of workers' health
- Periodic measurements of ambient air quality outside the plant area
- Overview recordkeeping of the health data of the neighboring residents
- Effective routine and preventive maintenance work plans for the equipment systems

8.2 IMPACT OF CHANGES IN BOILER OPERATION

The boiler characteristic curves presented in Section 5 are based on mean residence times and bulk temperatures. One variable, boiler load, is addressed. Other effects have been addressed in the model by the use of conservative temperatures and residence times. However, the normal fluctuations in boiler operation and maintenance can impact the final destruction efficiency of the waste.

The liquid waste being destroyed must be heated, then vaporized, before it can be burned. This is normally done by atomizing the waste into very small droplets. Typical oil atomizers achieve this through steam or air atomization, or by high-pressure mechanical atomization. A representative mean atomized droplet diameter is 80 μm. An upper bound of 200 μm is typical. A haphazard approach to waste atomization or poor atomizer maintenance would result in much larger droplet sizes. The results of poor atomization may be extrapolated from the consideration of the 80 and 200 μm droplets below.

In Section 6, estimates of the time required to vaporize droplets of dichlorobenzene were developed. For an 80-μm droplet the time requirement was approximately 0.05 sec. The 200 μm droplet required approximately 0.12 sec to vaporize. In Figure 36, the time required for vaporization is superimposed on the boiler full load characteristic curves. The important thing to note is that for the firetube boiler, the peak temperature has been passed before the droplet is vaporized. Going one step further, and considering that the residence time will vary from one half to twice the mean

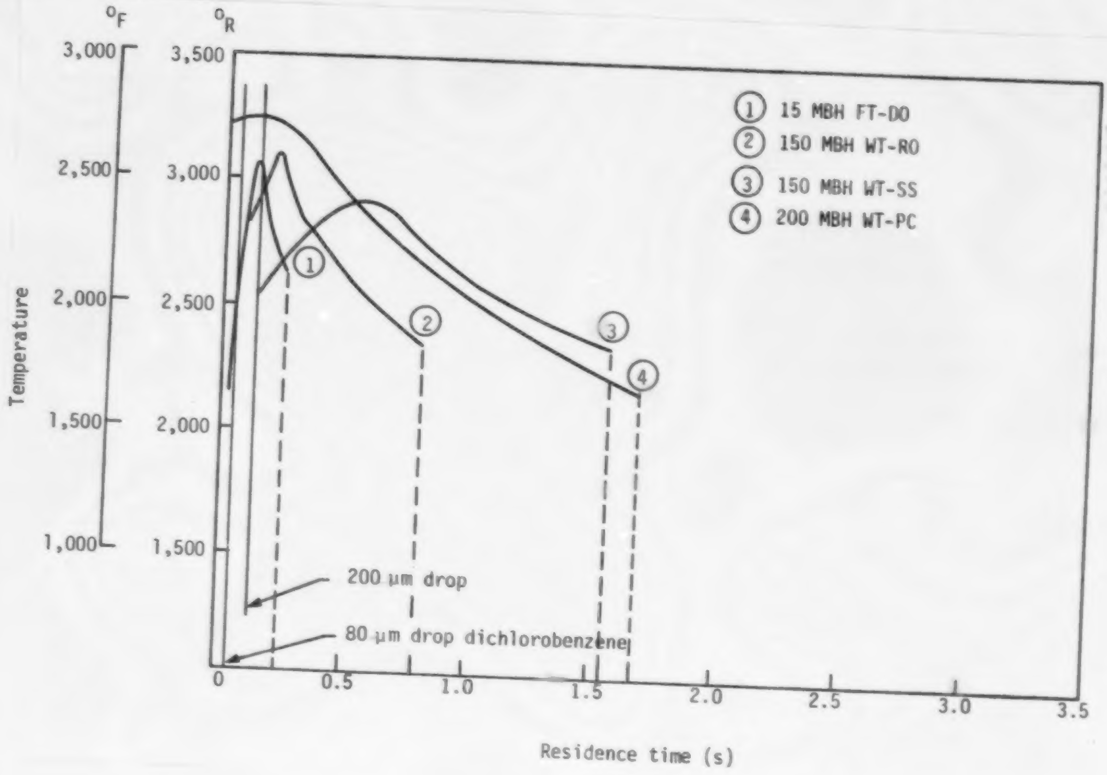

Figure 36. Effect of droplet size on vaporization times at full load.

residence time, waste may be leaving the furnace without being fully vaporized. With the rapid temperature drop after leaving the furnace, unreacted waste may be leaving the boiler. At full load, the residence time is approximately half the residence time at half load, as shown in Figure 37.

Other boiler operating and maintenance procedures may have similar impacts. Therefore, all procedures that would impact combustion conditions must be identified and procedures adopted to minimize the impacts.

Unfortunately, the effect of boiler operation at other than design conditions may result in the formation of products of incomplete combustion. The nature of these compounds may cause the bottom or flyash collected to be hazardous, or cause the generation of toxic air emissions.

8.3 BOILER RETROFIT TO ACCEPT HAZARDOUS WASTES COFIRED WITH A PRIMARY FUEL

If it is determined that the waste and boiler are theoretically compatible and that fugitive and secondary emissions are controllable, the final major area of concern is the retrofit requirements of the boiler itself. It is expected that this activity will represent a major economic impact. The following discussion outlines the major items of consideration.

8.3.1 Handling and Pretreatment of Waste

Combustion conditions, such as the temperture-time profile in industrial boiler furnaces discussed in Section 5, are of crucial importance for the effective disposal of hazardous waste in a boiler. However, the successful retrofit of an industrial boiler to accept and efficiently destroy hazardous wastes depends on a number of other major considerations. These considerations can be grouped into the following categories:

- Handling and pretreatment of waste
- Feeding and burning requirements
- Handling and posttreatment of residues, and
- Process control and inventory instrumentation

Handling and Pretreatment

Proper handling, storage, and feeding of hazardous wastes to a retrofitted industrial boiler is vital to reduce or eliminate exposure, spill, and contamination with adjoining surroundings (people and equipment systems) thereby ensuring the health and safety of the workers. Careful design of the facility including selection of equipment and process technology is important to meet the basic obligation of safe handling and proper disposal of hazardous wastes.

Handling and pretreatment of hazardous wastes consist of storage, transport, and preprocessing for injection into a boiler. The main environmental concerns in the storage and transport of hazardous wastes, and preprocessing equipment, is the danger posed by accidental spills, leaks from

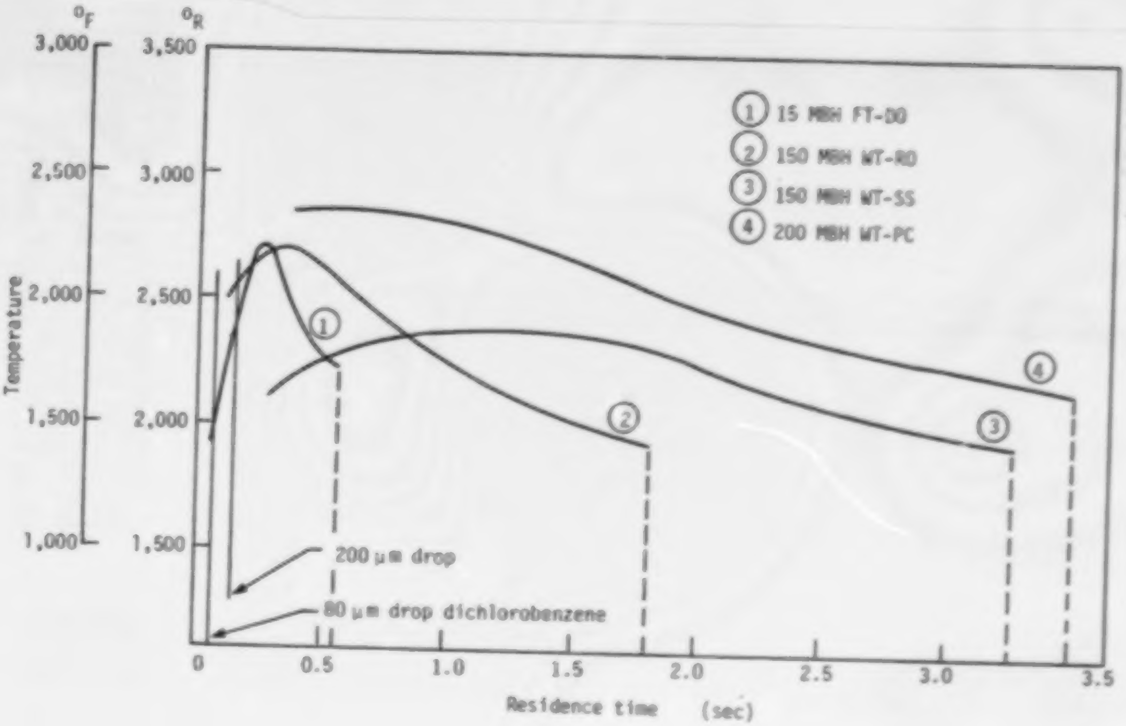

Figure 37. Effect of droplet size on vaporization times at half load.

piping, valves and joints, and possible breakdown of the material handling systems.

Preprocessing

Depending upon the nature of the hazardous waste and the type of industrial boiler in which the waste will be burned, it may be necessary that the "as-received" waste be processed before injection into the boiler. This preprocessing step for the pumpable wastes may involve heating, blending, screening, settling and other processing methods. Preprocessing of nonpumpable wastes, such as, sludge, solids, and containerized wastes may involve grinding, screening and shredding.

Heating

For highly viscous hazardous waste liquids, controlled steam heating with tank coils or in-line heaters have been used. Before the decision to heat the liquid is made, the flash point of the waste should be determined, and the heating device should be fitted with a set point temperature controller.

Blending

If the liquid cannot be heated, miscible liquid may be added to the viscous waste and blended to bring down the viscosity to pumpable or atomizing condition. However, the combination of two or more types of wastes in the mixture may produce sometimes uncontrolled and undesirable reactions, resulting in the formation of:

- Flammable substances
- Toxic fumes
- Explosive mixtures
- Complicated polymers
- Compounds of greater toxicity
- Compounds that may cause pressurization in closed vessels
- Shock and friction sensitive compounds

Where blending warrants extreme safety, the blending vessel may be blanketed with an inert gas and pneumatically-driven diaphragm feed pumps may be used to transport the liquid from storage tank to blender, and blender to boiler burner.

8.3.2 Feeding and Burning Requirements

The injection and combustion of hazardous waste in existing industrial boilers requires careful consideration of the boiler design, existing burners, potential retrofit of additional burners, as well as the typical operating cycle of the boiler.

The following types of atomization techniques may be used for liquid hazardous wastes:

- Rotating cup burner
- Mechanical or oil pressure air atomizing burner
- Steam or high-pressure air atomizing burner
- Low-pressure-air atomizing burner

For highly viscous hazardous wastes containing various amounts of noncombustible materials, steam or high-pressure air atomizing burners are preferred. For nonviscous highly organic wastes, mechanical low-pressure air or rotary cup burners may be used. Solid waste material can be injected with a pulverized fuel or dropped onto stoker grates.

Burner

The primary function for a properly designed burner is to transform the homogeneous liquid fuel to a finely atomized mist spray and to initiate turbulent mixing of combustion air with the finely atomized liquid fuel mist.

Boiler

The primary function of an industrial boiler is to supply steam flow as required by the plant process needs. One important consideration in a retrofit design to allow hazardous waste burning is that the steam supply rate of the boiler match the plant's steam requirements. From the fuel properties of the primary fossil fuel(s) and the quantity of available waste fuel, the portions of the total heat input to the boiler by the hazardous waste fuel and the auxiliary burner can be calculated.

The sensible heat loss in drying, heating, and bringing the hazardous waste to ignition point must be added to the heat input requirements for steam generation. Some of the hazardous wastes may contain 30 to 70 percent moisture, and thermal dissociation of the wastes may be required before the chemical heat from the hazardous waste fuel can be released. Appropriate proportioning of primary to waste fuels, together with minimum excess air supply and satisfactory burner design are key to achieving the desired thermal destruction of hazardous waste.

8.3.3 Posttreatment of Residues

Noncombustible residues discharged from an industrial boiler cofired with hazardous waste are associated with liquid and solid streams from pollution control devices and from the discharges from bottom and flyash hoppers.

Regulatory agencies will require the proper selection, operation and maintenance of pollution control devices by the industrial boiler operator burning hazardous wastes. Because of the heterogeneous characteristics of certain hazardous wastes, systems may be required to control both particulate and gaseous pollutants.

Proper selection of pollution control devices will require the following data of the flue gas stream:

- Flue gas volume, temperature, and particulate loading
- Estimated particle size distribution
- Composition of the flue gas
- Emission regulations

Particulate matter can be removed from the flue gas through the use of mechanical separators, electrostatic precipitators, or filtration devices. Gaseous pollutants can be removed by venturi, packed bed tower (or other gas-liquid contacting device), and mist eliminator assemblies, or by adsorption systems such as activated carbon. In some installations, a properly designed high energy scrubber and mist eliminator system may be adequate for controlling both particulate and gaseous pollutants. Monitoring the effluent gas stream discharged to the atmosphere is conducted to assure that the allowable pollutant concentrations are being maintained during normal operation.

8.3.4 Process Control and Monitoring Instrumentation

When an industrial boiler facility is retrofit to burn hazardous wastes, close monitoring of the entire facility may be required to continuously assure complete (99.99 percent) destruction. Such a monitoring system may cover all operations beginning with the transfer of wastes from storage tanks to valving, pumping, heating, agitating and feeding of the wastes to the boiler burners.

An important measurement in the boiler that is burning hazardous waste is the oxygen concentration in the flue gas. Stable combustion of a fuel generally occurs within a range of air-to-fuel ratios extending from the lean and rich limits of complete combustion and flame stability. An oxygen analyzer can be utilized to set the feed ratio to a level that will assure complete thermal destruction of the waste and efficient operation of the boiler.

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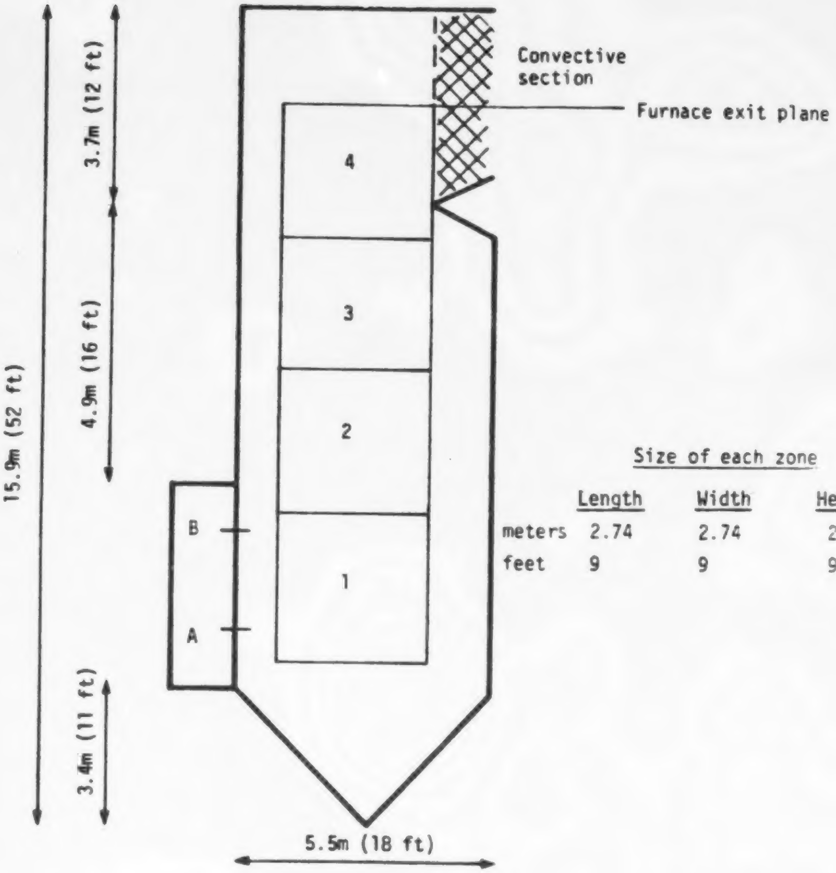
APPENDIX A

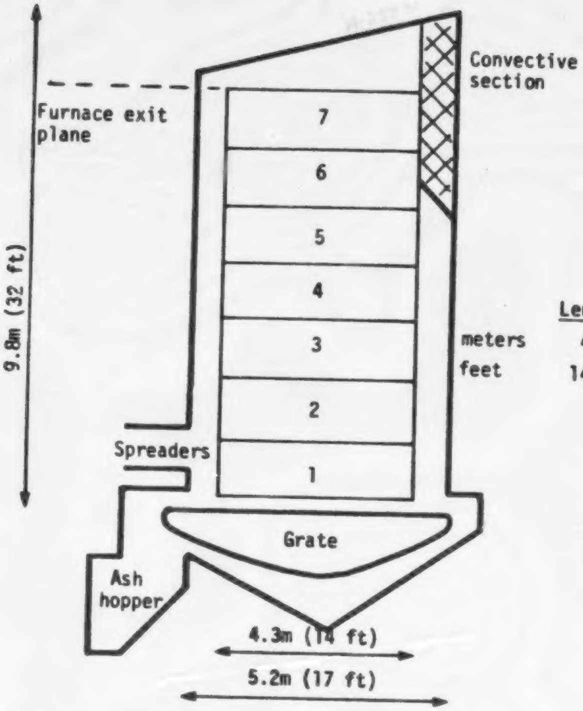
SCHEMATICS OF INDUSTRIAL BOILER TYPES SHOWING ISOTHERMAL ZONES

Figure	Title
A-1	Schematic of Pulverized-Coal-Fired Boiler, 58.6 MW (200 x million Btu/hr) -- Side View
A-2	Schematic of Coal-Fired Spreader Stoker Boiler, 44 MW (150 x million Btu/hr) -- Side View
A-3	Schematic of Residual-Oil-, Distillate-Oil-, and Natural-Gas-Fired Packaged Watertube Boiler, 44 MW (150 x million Btu/hr) -- Plan View
A-4	Schematic of Distillate-Oil- and Natural-Gas-Fired Firetube Boiler, 4.4 MW (15 x million Btu/hr) -- Plan View


Convective section
Furnace exit plane
15.9m (52 ft)
3.7m (12 ft)
4.9m (16 ft)
3.4m (11 ft)
4
3
2
1
B
A
5.5m (18 ft)

	Size of each zone		
	Length	Width	Height
meters	2.74	2.74	2.74
feet	9	9	9

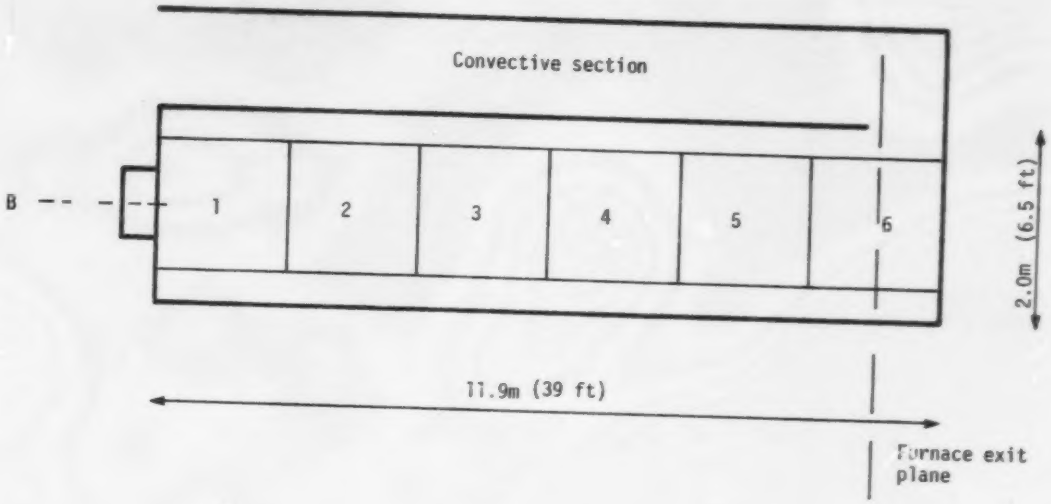
Figure A-1. Schematic of pulverized-coal-fired boiler, 58.6 MW (200 million Btu/hr) -- side view.


Convective section
Furnace exit plane
7
6
5
4
3
2
1
9.8m (32 ft)
Spreaders
Grate
Ash hopper
4.3m (14 ft)
5.2m (17 ft)

Size of each zone

	Length	Width	Height
meters	4.3	4.3	1.07
feet	14	14	3.5

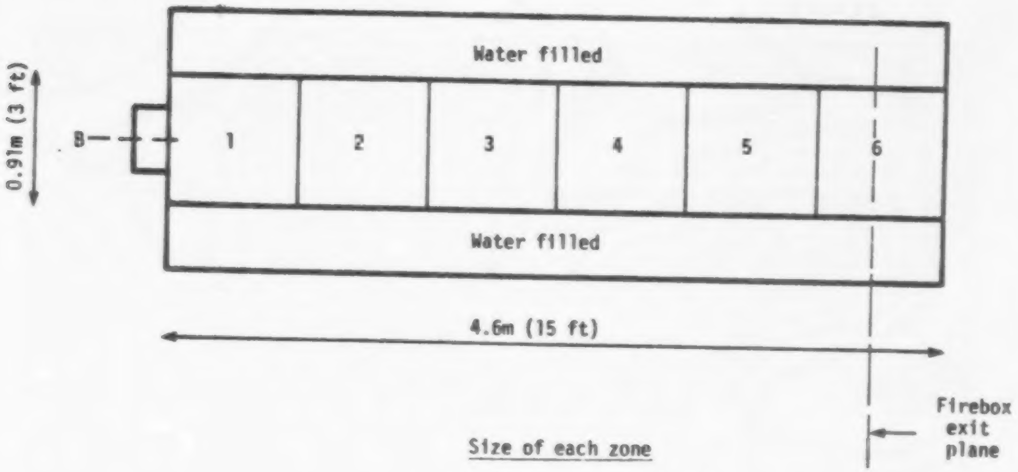
Figure A-2. Schematic of coal-fired spreader stoker boiler, 44 MW (150 million Btu/hr) -- side view.


Convective section
B
1
2
3
4
5
6
2.0m (6.5 ft)
11.9m (39 ft)
Furnace exit plane

Size of each zone

	Length	Width	Height
meters	1.83	1.83	1.83
feet	6	6	6

Figure A-3. Schematic of residual-oil-, distillate-oil-, and natural-gas-fired package watertube boiler, 44 MW (150 million Btu/hr) -- plan view


Water filled
0.91m (3 ft)
B
1
2
3
4
5
6
Water filled
4.6m (15 ft)
Firebox exit plane

Size of each zone

	Diameter	Length
meter	0.91	0.91
feet	3	3

Figure A-4. Schematic of distillate-oil- and natural-gas-fired firetube boiler, 4.4 MW (15 million Btu/hr) -- plan view

APPENDIX B

HEAT TRANSFER RESULTS -- COMPUTER LISTINGS

Table	Title
B-1	Heat Transfer Results -- Watertube Boiler Burning Pulverized Coal (Full Load)
B-2	Heat Transfer Results -- Watertube Boiler Burning Pulverized Coal (Half Load)
B-3	Heat Transfer Results -- Spreader Stoker (Full Load)
B-4	Heat Transfer Results -- Spreader Stoker (Half Load)
B-5	Heat Transfer Results -- Firetube Boiler Burning Distillate Oil (Full Load)
B-6	Heat Transfer Results -- Firetube Boiler Burning Distillate Oil (Half Load)
B-7	Heat Transfer Results -- Firetube Boiler Burning Natural Gas (Full Load)
B-8	Heat Transfer Results -- Firetube Boiler Burning Natural Gas (Half Load)
B-9	Heat Transfer Results -- Watertube Boiler Burning Residual Oil (Full Load)
B-10	Heat Transfer Results -- Watertube Boiler Burning Residual Oil (Half Load)
B-11	Heat Transfer Results -- Watertube Boiler Burning Natural Gas (Full Load)
B-12	Heat Transfer Results -- Watertube Boiler Burning Natural Gas (Half Load)
B-13	Heat Transfer Results -- Watertube Boiler Burning Distillate Oil (Full Load)
B-14	Heat Transfer Results -- Watertube Boiler Burning Distillate Oil (Half Load)

TABLE B-1. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING PULVERIZED COAL (FULL LOAD)

```
            ZONE                         1            2            3            4
---------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)        .610000-01   .610000-01   .610000-01   .610000-01

INLET AIR TEMP (DEG R)               860.000

TOTAL GAS FLOWRATE (LB/HR)           199140.
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)           .166456+09   .184951+08   .000000      .000000

GAS RECIRCULATION FROM 1
                       2             59742.0
                       3                          .000000
                       4                                       .000000
---------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)         3227.41      3172.80      2907.03      2690.11

NET RADIANT TRANSFER (BTU/HR)        .232898+08   .207604+08   .147808+08   .115009+08

NET CONVECTIVE TRANSFER (BTU/HR)     .283960+07   .275768+07   .241798+07   .215269+07

TOTAL HEAT INPUT (BTU/HR)            .186411+09   .225099+09   .155259+09   .138060+09

SENSIBLE HEAT GAIN (BTU/HR)          .160282+09   .201581+09   .138040+09   .124906+09

VELOCITY OF GASES (FT/SEC)           22.4983      22.1177      20.2650      18.7528

MEAN RESIDENCE TIME (SEC)            .400030      .406914      .444115      .479927

TOTAL RESIDENCE TIME (SEC)           1.73099

*FIN
```

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TABLE B-2. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING PULVERIZED COAL (HALF LOAD)

```
          ZONE                          1           2           3           4
-----------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)      .610000-01  .610000-01  .610000-01  .610000-01

INLET AIR TEMP (DEG R)             860.000

TOTAL GAS FLOWRATE (LB/HR)         113770.
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)         .832280+08  .924796+07  .000000     .000000

GAS RECIRCULATION FROM 1
                       2           34131.0
                       3                       .000000
                       4                                   .000000
-----------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)       2850.93     2750.96     2475.95     2258.98

NET RADIANT TRANSFER (BTU/HR)      .142339+08  .118241+08  .787121+07  .586190+07

NET CONVECTIVE TRANSFER (BTU/HR)   .234470+07  .221399+07  .186847+07  .160823+07

TOTAL HEAT INPUT (BTU/HR)          .945744+08  .109122+09  .732053+08  .634656+08

SENSIBLE HEAT GAIN (BTU/HR)        .779958+08  .950842+08  .634656+08  .559955+08

VELOCITY OF GASES (FT/SEC)         11.3541     10.9560     9.86069     8.99661

MEAN RESIDENCE TIME (SEC)          .792666     .821471     .912715     1.00038

TOTAL RESIDENCE TIME (SEC)         3.52723

*FIN
```

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TABLE B-3. HEAT TRANSFER RESULTS -- SPREADER STOKER (FULL LOAD)

ZONE	1	2	3	4	5	6	7
ABSORPTION COEFFICIENT (1/FT)	.500000-01	.900000-01	.500000-01	.400000-01	.300000-01	.200000-01	.200000-01
INLET AIR TEMP (DEG R)	810.000						
TOTAL GAS FLOWRATE (LB/HR)	157700.						
HEAT GAIN FROM CHEMICAL REACTION (BTU/HR)	.769758+08	.419868+08	.209954+08	.000000	.000000	.000000	.000000
GAS RECIRCULATION FROM 1							
2	55195.0						
3		.000000					
4			.000000				
5				.000000			
6					.000000		
7						.000000	
MEAN GAS TEMPERATURE (DEG R)	2487.11	2804.73	2911.45	2703.06	2550.33	2437.62	2355.20
NET RADIANT TRANSFER (BTU/HR)	.545516+07	.171055+08	.117721+08	.706206+07	.454904+07	.270740+07	.239454+07
NET CONVECTIVE TRANSFER (BTU/HR)	.291748+07	.357690+07	.380272+07	.337961+07	.305791+07	.281553+07	.258695+07
TOTAL HEAT INPUT (BTU/HR)	.913012+08	.161443+09	.125226+09	.109652+09	.992099+08	.916030+08	.860800+08
SENSIBLE HEAT GAIN (BTU/HR)	.829286+08	.140760+09	.109652+09	.992099+08	.916030+08	.860800+08	.810990+08
VELOCITY OF GASES (FT/SEC)	13.7298	15.4832	16.0724	14.9264	14.0788	13.4566	12.8912
MEAN RESIDENCE TIME (SEC)	.254920	.226051	.217765	.234484	.248600	.260095	.271502
TOTAL RESIDENCE TIME (SEC)	1.71342						

*FIN

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TABLE B-4. HEAT TRANSFER RESULTS -- SPREADER STOKER (HALF LOAD)

```
               ZONE                     1            2            3            4            5            6            7
--------------------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)      .500000-01   .900000-01   .500000-01   .400000-01   .300000-01   .200000-01   .200000-01

INLET AIR TEMP (DEG R)             810.000

TOTAL GAS FLOWRATE (LB/HR)         91100.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)         .349890+08   .209934+08   .699780+07   .699780+07   .000000      .000000      .000000

GAS RECIRCULATION FROM 1
                       2           31885.0
                       3                        .000000
                       4                                     .000000
                       5                                                  .000000
                       6                                                               .000000
                       7                                                                            .000000
--------------------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)       2105.50      2367.73      2356.52      2362.91      2189.65      2062.08      1947.48

NET RADIANT TRANSFER (BTU/HR)      .289604+07   .867418+07   .468035+07   .416825+07   .244400+07   .138808+07   .120359+07

NET CONVECTIVE TRANSFER (BTU/HR)   .215466+07   .267403+07   .264161+07   .265356+07   .230813+07   .205947+07   .184318+07

TOTAL HEAT INPUT (BTU/HR)          .431850+08   .758178+08   .547773+08   .544531+08   .476313+08   .428792+08   .394317+08

SENSIBLE HEAT GAIN (BTU/HR)        .381343+08   .644695+08   .474553+08   .476313+08   .428792+08   .394317+08   .363849+08

VELOCITY OF GASES (FT/SEC)         6.71448      7.55074      7.51498      7.53537      6.98284      6.57600      6.21006

MEAN RESIDENCE TIME (SEC)          .521262      .463531      .465787      .464476      .501229      .532239      .563506

TOTAL RESIDENCE TIME (SEC)         3.51203

*FIN
```

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TABLE B-5. HEAT TRANSFER RESULTS -- FIRETUBE BOILER BURNING DISTILLATE OIL (FULL LOAD)

```
        ZONE                             1           2           3           4           5           6
---------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)        .650000     .550000     .350000     .250000     .200000     .150000

INLET AIR TEMP (DEG R)               640.000

TOTAL GAS FLOWRATE (LB/HR)           14420.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)           .600240+07  .600240+07  .300120+07  .000000     .000000     .000000

GAS RECIRCULATION FROM 1
                       2             4326.00
                       3                         .000000
                       4                                     .000000
                       5                                                 .000000
                       6                                                             .000000
---------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)         2150.37     2832.29     3077.51     2877.14     2752.02     2622.99

NET RADIANT TRANSFER (BTU/HR)        522623.     .160203+07  .166628+07  954902.     658813.     470380.

NET CONVECTIVE TRANSFER (BTU/HR)     45000.8     72872.1     82630.7     74420.4     68773.6     64844.0

TOTAL HEAT INPUT (BTU/HR)            .673997+07  .153263+08  .135010+08  .117521+08  .107228+08  .999522+07

SENSIBLE HEAT GAIN (BTU/HR)          .617234+07  .136534+08  .117521+08  .107228+08  .999522+07  .946000+07

VELOCITY OF GASES (FT/SEC)           43.3302     57.0710     62.0123     57.9748     55.0507     52.8536

MEAN RESIDENCE TIME (SEC)            .376964-01  .438051-01  .403146-01  .431222-01  .454127-01  .473005-01

TOTAL RESIDENCE TIME (SEC)           .277651

*FIN
```

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TABLE B-6. HEAT TRANSFER RESULTS -- FIRETUBE BOILER BURNING DISTILLATE OIL (HALF LOAD)

```
              ZONE                      1           2           3           4           5           6
------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)       .650000     .550000     .350000     .250000     .200000     .150000

INLET AIR TEMP (DEG R)              640.000

TOTAL GAS FLOWRATE (LB/HR)          7635.00
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)          .300120+07  .300120+07  .150060+07  .000000     .000000     .000000

GAS RECIRCULATION FROM 1
                       2            763.500
                       3                        .000000
                       4                                    .000000
                       5                                                .000000
                       6                                                            .000000
------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)        1908.38     2575.35     2730.10     2499.97     2340.42     2224.69

NET RADIANT TRANSFER (BTU/HR)       315240.     .109824+07  .102626+07  542208.     354290.     241785.

NET CONVECTIVE TRANSFER (BTU/HR)    35087.7     62163.5     68404.2     59115.3     52839.2     48415.4

TOTAL HEAT INPUT (BTU/HR)           .338842+07  .652657+07  .637949+07  .528483+07  .468350+07  .427638+07

SENSIBLE HEAT GAIN (BTU/HR)         .303809+07  .536616+07  .528483+07  .468350+07  .427638+07  .398617+07

VELOCITY OF GASES (FT/SEC)          20.3604     27.4763     29.1274     26.6720     24.9699     23.7351

MEAN RESIDENCE TIME (SEC)           .122787     .909874-01  .858299-01  .937311-01  .100121     .105329

TOTAL RESIDENCE TIME (SEC)          .598786

*FIN
```

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TABLE B-7. HEAT TRANSFER RESULTS -- FIRETUBE BOILER BURNING NATURAL GAS (FULL LOAD)

```
            ZONE                       1            2            3            4            5            6
-----------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)       .280000      .250000      .200000      .180000      .100000+00   .800000-01

INLET AIR TEMP (DEG R)              640.000

TOTAL GAS FLOWRATE (LB/HR)          13255.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)          .749975+07   .599980+07   .149995+07   .000000      .000000      .000000

GAS RECIRCULATION FROM 1
                       2            3976.50
                       3                         1988.25
                       4                                      .000000
                       5                                                   .000000
                       6                                                                .000000
-----------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)        2569.62      3262.77      3267.90      3051.81      2931.58      2838.57

NET RADIANT TRANSFER (BTU/HR)       639188.      .168032+07   .137661+07  962740.       496775.      367861.

NET CONVECTIVE TRANSFER (BTU/HR)    61850.7      90445.8      90720.1      81599.1      76364.3      72187.9

TOTAL HEAT INPUT (BTU/HR)           .816424+07   .169760+08   .149536+08   .117249+08   .106805+08   .101074+08

SENSIBLE HEAT GAIN (BTU/HR)         .746320+07   .152053+08   .134863+08   .106805+08   .101074+08   .966788+07

VELOCITY OF GASES (FT/SEC)          47.5951      60.4358      60.5288      56.5262      54.2994      52.3768

MEAN RESIDENCE TIME (SEC)           .525264-01   .413676-01   .413027-01   .442273-01   .460410-01   .475497-01

TOTAL RESIDENCE TIME (SEC)          .273015

*FIN
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TABLE B-8. HEAT TRANSFER RESULTS -- FIRETUBE BOILER BURNING NATURAL GAS (HALF LOAD)

```
                ZONE                    1          2          3          4          5          6
------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)       .280000    .250000    .200000    .180000    .100000+00 .800000-01

INLET AIR TEMP (DEG R)              6[illegible]0.000

TOTAL GAS FLOWRATE (LB/HR)          7021.50
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)          .374987+07 .299990+07 749975.    .000000    .000000    .000000

GAS RECIRCULATION FROM 1
                       2            2106.45
                       3                       1053.22
                       4                                  .000000
                       5                                             .000000
                       6                                                        .000000
------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)        2367.82    2934.74    2880.47    2637.41    2504.07    2402.26

NET RADIANT TRANSFER (BTU/HR)       469306.    .111158+07 829950.    532252.    262338.    107828.

NET CONVECTIVE TRANSFER (BTU/HR)    55697.2    77304.4    74924.7    64615.1    80871.6    84439.8

TOTAL HEAT INPUT (BTU/HR)           .409921+07 .819237+07 .692361+07 .528232+07 .463546+07 .431425+07

SENSIBLE HEAT GAIN (BTU/HR)         .357621+07 .700349+07 .601878+07 .463546+07 .431425+07 .407198+07

VELOCITY OF GASES (FT/SEC)          23.2273    28.7947    28.2623    25.8774    24.3691    23.5702

MEAN RESIDENCE TIME (SEC)           .107632    .868214-01 .884872-01 .966096-01 .101704    .106066

TOTAL RESIDENCE TIME (SEC)          .587840

*FIN
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TABLE B-9. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING RESIDUAL OIL (FULL LOAD)

```
               ZONE                      1           2           3           4           5           6
-------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)        .350000     .300000     .200000     .150000     .120000     .120000

INLET AIR TEMP (DEG R)               810.000

TOTAL GAS FLOWRATE (LB/HR)           136500.
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)           .965692+08  .413868+08  .000000     .000000     .000000     .000000

GAS RECIRCULATION FROM 1
                       2             54632.0
                       3                         54632.0
                       4                                     .000000
                       5                                                 .000000
                       6                                                             .000000
-------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)         2833.58     3057.30     2856.88     2666.76     2524.46     2397.37

NET RADIANT TRANSFER (BTU/HR)        .147711+08  .207108+08  .106590+08  .674032+07  .480818+07  .394407+07

NET CONVECTIVE TRANSFER (BTU/HR)     .207276+07  .228244+07  .210424+07  .193272+07  .180338+07  .168781+07

TOTAL HEAT INPUT (BTU/HR)            .108815+09  .176443+09  .149662+09  .976013+08  .889282+08  .825567+08

SENSIBLE HEAT GAIN (BTU/HR)          .919709+08  .153449+09  .136899+09  .889282+08  .825567+08  .769048+08

VELOCITY OF GASES (FT/SEC)           45.3901     48.9739     45.7634     42.7179     40.4584     38.4027

MEAN RESIDENCE TIME (SEC)            .132108     .122514     .131109     .140456     .148374     .156289

TOTAL RESIDENCE TIME (SEC)                                                                       .830850

*FIN
```

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TABLE B-10. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING RESIDUAL OIL (HALF LOAD)

```
          ZONE                     1          2          3          4          5          6
---------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)   .350000    .300000    .200000    .150000    .120000    .120000

INLET AIR TEMP (DEG R)          810.000

TOTAL GAS FLOWRATE (LB/HR)      72290.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)      .482846+08 .206954+08 .000000    .000000    .000000    .000000

GAS RECIRCULATION FROM 1
                       2        28916.0
                       3                   28916.0
                       4                              .000000
                       5                                         .000000
                       6                                                    .000000
---------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)    2556.86    2681.36    2448.31    2237.09    2082.63    1950.66

NET RADIANT TRANSFER (BTU/HR)   .987122+07 .123078+08 .577938+07 .334109+07 .210783+07 .168182+07

NET CONVECTIVE TRANSFER (BTU/HR) .182815+07 .195668+07 .175249+07 .156006+07 .141601+07 .128983+07

TOTAL HEAT INPUT (BTU/HR)       .547448+08 .829076+08 .664290+08 .419425+08 .370413+08 .335175+08

SENSIBLE HEAT GAIN (BTU/HR)     .430454+08 .686431+08 .588971+08 .370413+08 .335175+08 .305463+08

VELOCITY OF GASES (FT/SEC)      21.6782    22.7338    20.7579    18.9670    17.6575    16.5385

MEAN RESIDENCE TIME (SEC)       .276776    .263924    .289046    .316338    .339799    .362789

TOTAL RESIDENCE TIME (SEC)
                                                                                       1.84867
*FIN
```

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TABLE B-11. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING NATURAL GAS (FULL LOAD)

ZONE	1	2	3	4	5	6
ABSORPTION COEFFICIENT (1/FT)	.200000	.150000	.120000	.100000+00	.900000-01	.800000-01
INLET AIR TEMP (DEG R)	810.000					
TOTAL GAS FLOWRATE (LB/HR)	125120.					
HEAT GAIN FROM CHEMICAL REACTION (BTU/HR)	.700740+08	.490518+08	.210222+08	.000000	.000000	.000000
GAS RECIRCULATION FROM 1						
2	37536.					
3		37536.0				
4			25024.0			
5				.000000		
6					.000000	
MEAN GAS TEMPERATURE (DEG R)	2605.56	3205.57	3271.96	3059.98	2889.10	2735.11
NET RADIANT TRANSFER (BTU/HR)	.740502+07	.145404+08	.131164+08	.870307+07	.510576+07	.440699+07
NET CONVECTIVE TRANSFER (BTU/HR)	.186985+07	.239343+07	.244557+07	.226556+07	.212122+07	.199430+07
TOTAL HEAT INPUT (BTU/HR)	.806012+08	.151626+09	.156494+09	.128472+09	.979339+08	.907069+08
SENSIBLE HEAT GAIN (BTU/HR)	.713264+08	.134692+09	.140930+09	.117503+09	.907069+08	.843056+08
VELOCITY OF GASES (FT/SEC)	38.2355	47.0403	48.0147	44.9040	42.3964	40.1366
MEAN RESIDENCE TIME (SEC)	.156922	.127550	.124962	.133619	.141522	.149490
TOTAL RESIDENCE TIME (SEC)						.834064

*FIN

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TABLE B-12. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING NATURAL GAS (HALF LAOD)

```
          ZONE                          1          2          3          4            5            6
------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)       .200000    .150000    .120000    .100000+00   .800000-01   .600000-01

INLET AIR TEMP (DEG R)              810.000

TOTAL GAS FLOWRATE (LB/HR)          68060.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)          .350370+08 .245259+08 .105111+08 .000000      .000000      .000000

GAS RECIRCULATION FROM 1
                       2            20418.0
                       3                       20418.0
                       4                                  13612.0
                       5                                             .000000
                       6                                                          .000000
------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)        2347.59    2819.61    2831.05    2604.56      2418.93      2256.29

NET RADIANT TRANSFER (BTU/HR)       .502166+07 .875050+07 .719472+07 .437970+07   .239674+07   .195482+07

NET CONVECTIVE TRANSFER (BTU/HR)    .165076+07 .205883+07 .205039+07 .184922+07   .169130+07   .155761+07

TOTAL HEAT INPUT (BTU/HR)           .407645+08 .729487+08 .725844+08 .575468+08   .428458+08   .387577+08

SENSIBLE HEAT GAIN (BTU/HR)         .340921+08 .621394+08 .633393+08 .513179+08   .387577+08   .352453+08

VELOCITY OF GASES (FT/SEC)          18.7376    22.5071    22.5985    20.7905      19.5008      18.0105

MEAN RESIDENCE TIME (SEC)           .320211    .266582    .265505    .288593      .310740      .333140

TOTAL RESIDENCE TIME (SEC)
                                                                                               1.78477
FIN
```

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TABLE B-13. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING DISTILLATE OIL (FULL LOAD)

```
      ZONE                             1          2          3          4          5          6
--------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)      .350000    .300000    .150000    .120000    .100000+00 .100000+00

INLET AIR TEMP (DEG R)             840.000

TOTAL GAS FLOWRATE (LB/HR)         162540.
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)         .965874+08 .413946+06 .000000    .000000    .000000    .000000

GAS RECIRCULATION FROM 1
                       2           53016.0
                       3                      53016.0
                       4                                 .000000
                       5                                            .000000
                       6                                                       .000000

--------------------------------------------------------------------------------------------------
MEAN GAS TEMPRATURE (DEG R)        2864.62    3089.95    2919.47    2740.86    2601.06    2476.50

NET RADIANT TRANSFER (BTU/HR)      .157166+08 .216018+08 .854461+07 .596830+07 .428074+07 .367238+07

NET CONVECTIVE TRANSFER (BTU/HR)   .204725+07 .230580+07 .215157+07 .198993+07 .186161+07 .174552+07

TOTAL HEAT INPUT (BTU/HR)          .108486+09 .174366+09 .147266+09 .974654+08 .895071+08 .833648+08

SENSIBLE HEAT GAIN (BTU/HR)        .906745+08 .150459+09 .136570+09 .895071+08 .833648+08 .779471+08

VELOCITY OF GASES (FT/SEC)         44.5500    48.0328    45.3826    42.6062    40.4550    38.4936

MEAN RESIDENCE TIME (SEC)          .134741    .124915    .132209    .140825    .148394    .155870

TOTAL RESIDENCE TIME (SEC)                                                                .836955

*FIN
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TABLE B-14. HEAT TRANSFER RESULTS -- WATERTUBE BOILER BURNING DISTILLATE OIL (HALF LOAD)

```
        ZONE                           1            2            3            4            5            6
-------------------------------------------------------------------------------------------------------------
ABSORPTION COEFFICIENT (1/FT)      .350000      .300000      .150000      .120000     .100000+00  .100000+00

INLET AIR TEMP (DEG R)             810.000

TOTAL GAS FLOWRATE (LB/HR)         71770.0
HEAT GAIN FROM
CHEMICAL REACTION (BTU/HR)         .482437+08  .206975+08  .000000      .000000      .000000      .000000

GAS RECIRCULATION FROM 1
                       2           28708.0
                       3                        28708.0
                       4                                     .000000
                       5                                                  .000000
                       6                                                               .000000
-------------------------------------------------------------------------------------------------------------
MEAN GAS TEMPERATURE (DEG R)       2554.86      2706.57      2518.89      2318.91      2162.14      2023.63

NET RADIANT TRANSFER (BTU/HR)      .100657+08  .120741+08  .451770+07  .298504+07  .205495+07  .170749+07

NET CONVECTIVE TRANSFER (BTU/HR)   .182573+07  .194299+07  .178196+07  .161413+07  .148479+07  .137250+07

TOTAL HEAT INPUT (BTU/HR)          .547081+08  .823959+08  .666438+08  .431972+08  .385981+08  .350583+08

SENSIBLE HEAT GAIN (BTU/HR)        .428167+08  .683789+08  .603442+08  .385981+08  .350583+08  .319783+08

VELOCITY OF GASES (FT/SEC)         21.5054      22.7625      21.2027      19.5193      18.1998      17.0338

MEAN RESIDENCE TIME (SEC)          .278999      .263361      .282985      .307387      .329675      .352240

TOTAL RESIDENCE TIME (SEC)
                                                                                                    1.81465
*FIN
```

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APPENDIX C

MODEL APPLICATION -- AN EXAMPLE CASE

This appendix demonstrates the application of the model developed in Section 7. The example case is a test burn of PCB's in an industrial boiler owned and operated by General Motors Corporation at their Bay City, Michigan facility. The test program was carried out by GCA/Technology Division under U.S. Environmental Protection Agency Contract No. 68-02-3168, Work Assignment No. 9. The work was completed October 31, 1980. The test report is "Evaluation of PCB Destruction Efficiency in an Industrial Boiler," EPA-600/2-81-055a.

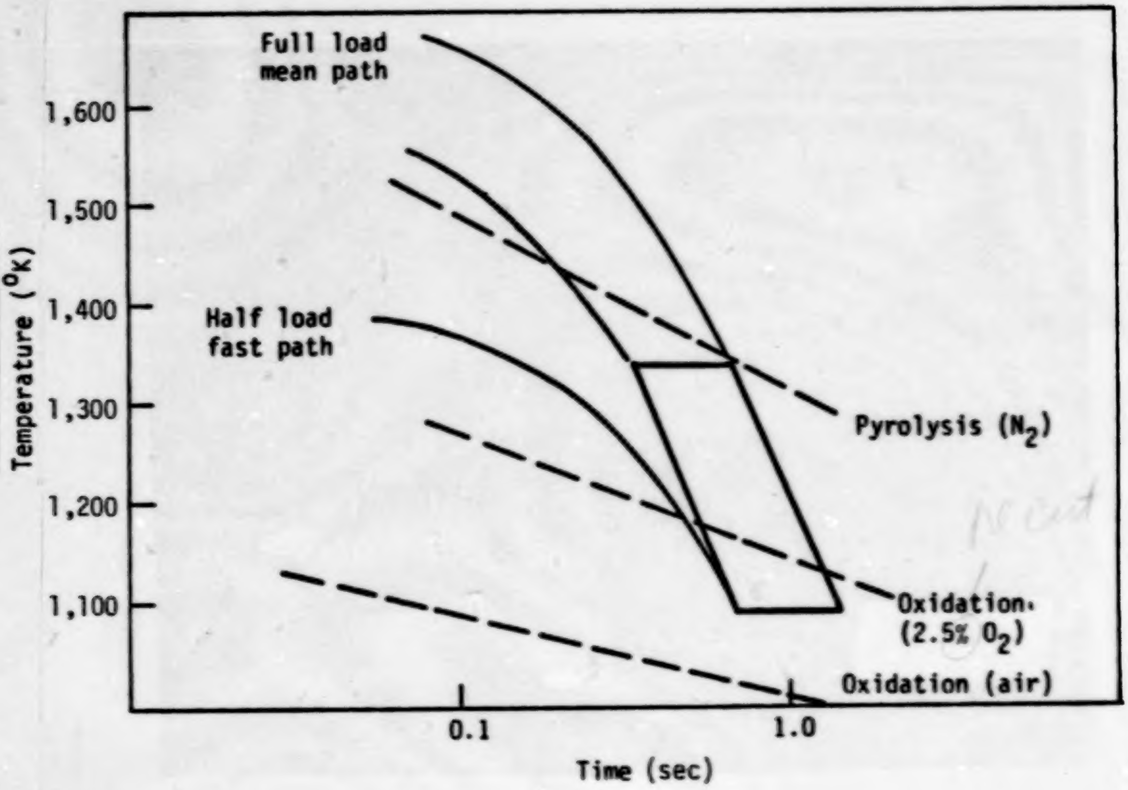
The boiler was a 60 million Btu/hr package water tube unit burning no. 6 distillate oil. The waste stream was waste oil containing approximately 500 ppm Arochlor 1254. The waste stream and oil were mixed in a ratio of 1:10 prior to injection. The boiler was operated at half load (i.e., the fuel injection rate was half the maximum rate).

The time and temperature profile within the fire box was generated with the Acurex Zonal Heat Balance Program. Kinetic data were derived from thermal destruction unit data on 2, 2', 4, 5, 5'-pentachlorobiphenyl generated by Duvall at the University of Dayton Research Institute (Ref. 50).

The model input data is summarized in Table 1, and the predictive model diagram is shown in Figure 1. The model predicts that for half load and 2.5 percent O_2 content the boiler should achieve greater than 99.99 percent destruction. The test results are given in Table 2 and confirm this prediction.

Table C-1. INPUT PARAMETERS FOR EXAMPLE CASE MODEL APPLICATION

Compound (2,2', 4, 5, 5' - Pentachlorobiphenyl)			
	Pyrolysis	Oxidation (2.5% O_2)	Oxidation (21% O_2)
E (Kcal/g-mole)	53.6	66.7 ± 0.5	70.0
A (sec^{-1})	7.44×10^{9}	2.6×10^{12}	1.10×10^{16}
Boiler			
T_m	1700°K ±50°	(Flame)	
T_x	1144°K ±50°	(Back wall)	
t_m	0.4 sec	Acurex boiler zonal heat balance	
t_x	1.8 sec		
(O_2% in flue gas	6^{+}%)		



No cut

Figure C-1. Predicted boiler operational zone and destruction efficiency curves for example case.

Table C-2. REPORTED DESTRUCTION EFFICIENCY OF PCB's IN AN INDUSTRIAL BOILER

Run number	PCB in fuel[a] concentration range (mg/kg)	PCB[b] in (mg/min)	PCB out (mg/min)	PCB[c] destruction efficiency (%)
PCB-2	34-72	480-1,000	5.8×10^{-2}	≥ 99.99[d]
PCB-3	34-76	480-1,100	5.6×10^{-2}	≥ 99.99[d]
PCB-4	34-76	480-1,100	5.6×10^{-2}	≥ 99.99[d]

Note: Density of 1:10 Dilution of Waste Oil: No. 6 fuel oil is 3.4 kg/gal.

[a] Based on GM and GCA reported results.

[b] Fuel combustion rate: 3.43 kg/gal x 4 gal/min fuel flow = 14 kg/min.

[c] Percent destruction = 100 $\frac{\text{PCB in - PCB out}}{\text{PCB in}}$

[d] This assumes 100 percent sample collection efficiency. A validated test sample collection efficiency was not conducted as part of this verification burn.